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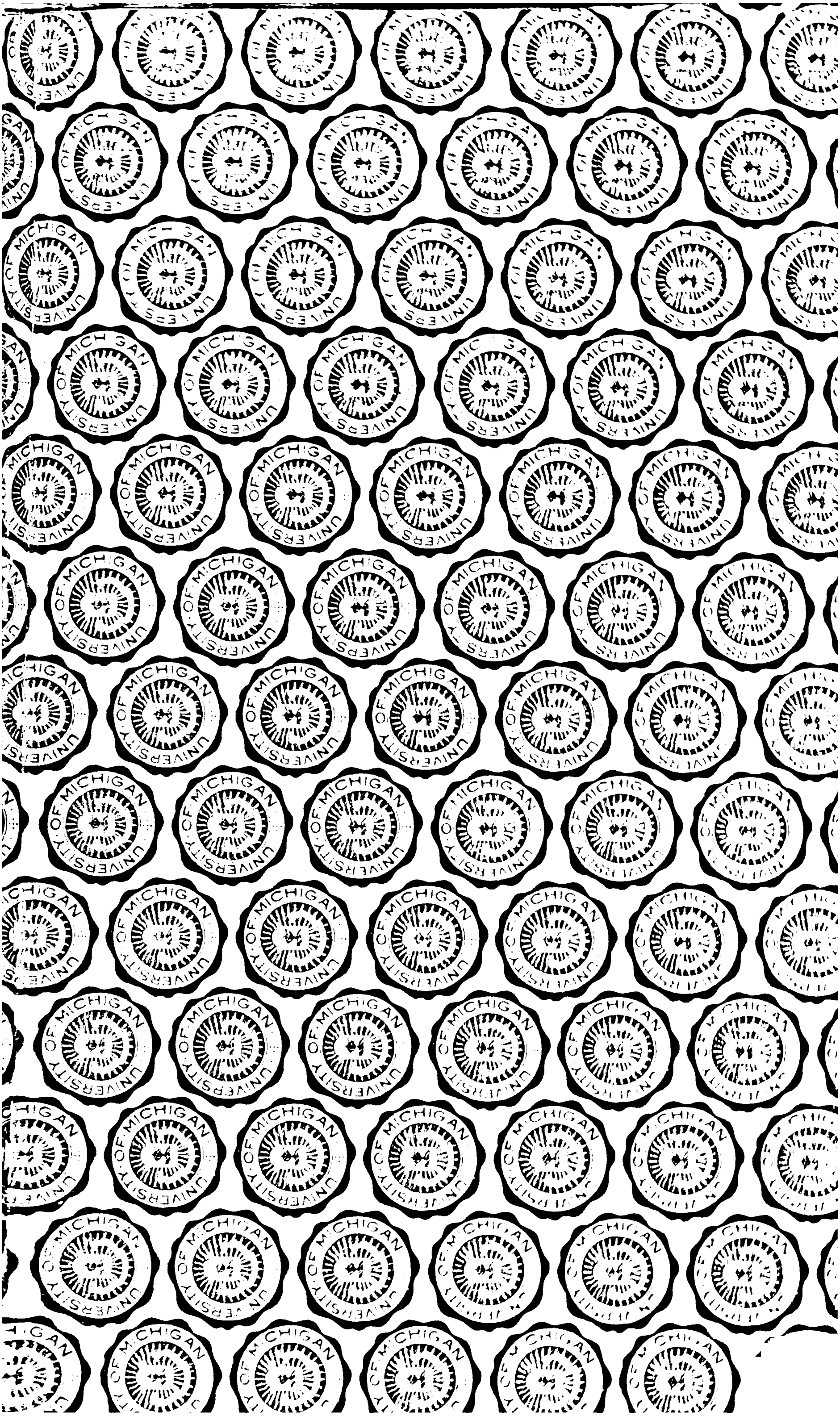

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THE DYNAMICS OF SURFACES

THE DYNAMICS OF SURFACES

AN INTRODUCTION TO THE STUDY OF BIOLOGICAL SURFACE PHENOMENA

BY

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ABBREVIATIONS IN TITLES OF JOURNALS

Ann. Chim. Phys.	Annales de chimie et de physique.
Ann. Physik.	Annalen der Physik.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Biochem. Zeits.	Biochemische Zeitschrift.
Comptes rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
J. C. S.	Journal of the Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
Kolloid. Zeits.	Zeitschrift für Chemie und Industrie der Kolloide.
Pflüger's Arch.	Archiv für die gesamte Physiologie des Menschen und der Thiere.
Phil. Mag.	The Philosophical Magazine.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Z. Elektroch.	Zeitschrift für Elektrochemie.
Z physik. Chem.	Zeitschrift für physikalische Chemie.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

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AUTHOR'S PREFACE

The forces which are localised in surfaces play a much greater part in biological processes than has previously been suspected, and the recognition of this fact has recently spread very rapidly over biological literature. On the one hand, the accumulation of facts proceeds rapidly, while on the other hand, the theoretical treatment of surface reactions is developing extremely slowly. The theoretical development is naturally concerned in the first place with the simplest conditions, and cannot be extended without modification to biological problems. The biological data, on the contrary, are generally obtained under very complicated, and to some extent fundamentally different, conditions. The best illustration of this fact is the confusion which has become associated with the idea of adsorption, owing to the assumption that the theory of purely mechanical adsorption could be extended to biological processes, in which, as a matter of fact, it does not apply.

This little book is intended to summarise the essential points in the theoretical treatment of surface phenomena, always keeping in view the object of applying the knowledge obtained for biological purposes. Although not a biological work, it is intended for biologists and it is written from their point of view. Some of their special problems (*e.g.* the specific reactions of ferments and toxins in the widest sense) can only be solved by investigations into surface conditions. These problems, however, are at most only touched upon, since their details are already familiar to those who are interested. The object of the book is rather to give an account of the principles of surface reactions, so as to enable biologists to deal with such problems more fundamentally than they have done hitherto. An attempt must be made to unify the theoretical conceptions, otherwise we shall have only a mass of isolated facts without any inner meaning. If the attempt still leaves something to be desired, there is nothing to prevent the defects from being remedied and the theory perfected by general discussion.

L. MICHAELIS.

BERLIN,
May 1*st*, 1909.

THE
DYNAMICS OF SURFACES

CHAPTER I

INTRODUCTORY

1. **The General Conception of a Surface.**—When the tiny primitive cells from which all higher organisms rise, begin to increase their mass in the course of their growth, the increase does not take place by the simple enlargement of a single cell, but by incessant division of the cells. Partition walls are formed, and the surface increases out of all proportion to the mass. The new surface is partly external, enormously developed by the formation of folds, crevices, and cavities, and partly internal, consisting of the walls or partitions which bound the individual cells. The significance of this process of growth has been partly understood for a long time, since it has long been recognised that the exchange of material between the living mass and its surroundings is assisted considerably by the great development of the surface. Recently, however, it has begun to be realised that the expansion of the surfaces has another quite different function. The exchange of material is merely favoured

by large surfaces and would still proceed, though of course more slowly, with smaller ones. But every surface is also the seat of special forces, principally mechanical and electrical, and it is these forces which we intend to study in detail.

As a starting-point, however, a clear definition of the term *surface* in the physico-chemical sense is necessary. The most satisfactory formula is to define a surface as the boundary between two phases. The meaning of the term *phase*, originally used by Willard Gibbs, will be best explained by the following example.

Consider a fixed mass of a simple chemical substance e.g. water, which is enclosed partly by the walls of the containing vessel and partly by the air. This quantity of water is called a chemical system. If we now imagine the system to be divided by numerous partitions into single particles, then the chemical and physical composition of all the particles is identical. The system is, therefore, described as homogeneous. If the imaginary process of subdivision could be carried sufficiently far the homogeneity would reach a limit, since, according to the molecular hypothesis, all substances consist of molecules separated from each other by empty interspaces. Therefore, by the use of sufficiently close partitions, we must reach an irregular subdivision of all substances, where one enclosed space may contain a single molecule and another may be entirely empty. In this sense, therefore, there is, strictly speaking, no such thing as a homogeneous system. But if we do not assume the subdivision to continue till we have reached molecular dimensions, we can, relatively speaking, describe the water as a homogeneous system. Such systems are obtained, not only with pure chemical compounds, such as water, but also with such mixtures as salt solutions, in which, so long as we do not subdivide into molecules, every portion has the same chemical composition and physical properties. On the other hand, a single chemical substance does not always form a homogeneous system. Water can exist in the three states of aggregation, ice, liquid, and vapour, side by side. If a chemical system composed of water in these three forms be divided into small particles, there will now be three kinds of particle with different physical properties. The system is therefore described as heterogeneous, and each single homogeneous portion of it is called a *phase*, the boundaries between different phases being described as surfaces.

In the above arguments one very important assumption has been made, namely, that the chemical system which we have been dividing into phases is in equilibrium. This means that all changes which can proceed spontaneously without requiring external energy (*e.g.* diffusion, distribution of heat, chemical reactions, equalisation of pressure) have already ceased. If the system has not yet reached equilibrium, it is possible that the compositions of single particles in different parts of the system may differ, without its being necessary to distinguish different phases. A salt solution, for instance, which has different concentrations in different portions of the solution, only lacks homogeneity because the spontaneous interchange of material, called diffusion, has not yet ceased. The difference between this kind of heterogeneity and the other is summarised as follows. In a system which is not in equilibrium the variation of composition is continuous, *i.e.* portions of the system which are infinitely near together have only an infinitely small difference in their composition. At the boundary between two phases there is discontinuity, and portions of the system which are only an immeasurably small distance apart have a measurable difference in composition, *i.e.* there is a sharply defined boundary which we call a surface.

CHAPTER II

THE SURFACE AS THE SEAT OF MECHANICAL FORCES

2. **Surface Tension.**—The force of gravity is always associated with the presence of mass, and we cannot conceive of the existence of one without the other. If we add to the mass of a chemical system we produce a corresponding increase in its weight or gravitational force. In the same way the surface is always the seat of special forces, and when the extent of the surface is increased the magnitude of these forces is increased. The great difference between the cases of gravity and of surface force is, that the mass of a system cannot be increased except by addition of matter, whereas the surface can be increased without any material addition to the system. In the heterogeneous system water-chloroform, for instance, the boundary between the two phases in the stationary condition is a simple horizontal surface. When the liquid is shaken, however, the chloroform is divided into small drops, and the boundary between the two phases is greatly increased. The total surface energy must consequently be increased also, at the expense of some other form of energy, such as heat. The characteristic force which is acting in all surfaces is called *surface tension*, and the form of energy to which it belongs is called by

W. Ostwald[1] surface energy. Before discussing the relations between surface tension and surface energy it is well to develop a clear picture of surface tension starting from the usual conceptions of matter.

It is desirable to limit ourselves at first to the surface tensions of liquids, since these are most easily understood and can be determined experimentally. A liquid consists of molecules which exert upon each other an attractive force. This force is necessary to explain why the molecules do not become separated from each other by infinite distances. If we consider a single molecule in the interior of the liquid, we recognise that it is attracted by neighbouring molecules with the same intensity in all directions. Thus the single molecule is subjected on all sides to an internal pressure of thousands of atmospheres, which, however, being uniform in all directions, does not produce any effect other than that of keeping the liquid particles together, the result being the property which is called the cohesion of the liquid. The molecules which are located in the surface are subject to different conditions. They are attracted towards the interior of the liquid by the molecules situated there, but there is no similar attraction towards the exterior. The effect produced is therefore the same as if the outer layer of liquid were subjected to a high pressure (perpendicular to the surface). This pressure has two consequences: first, since liquids possess a distinct (though small) compressibility, the outer film will consist of a layer of compressed liquid; and second, since all the particles in the surface are being strongly attracted towards the interior, the surface will always have a tendency to become reduced to the smallest possible dimensions.

---

[1] Wilhelm Ostwald, *Lehrbuch der theoretischen Chemie*, I, 1.

If we place a liquid into a position where it is not affected by gravity (*e.g.* by suspending it in another liquid of the same density, with which it does not mix), the form of the liquid changes until it possesses the smallest possible surface for the given volume. The form in which this condition is satisfied can be shown geometrically to be the sphere. The surface of a liquid behaves, therefore, as if it consisted of a stretched sheet of rubber. The analogy, however, is not quite perfect. If a rubber balloon filled with water be distorted into any non-spherical shape, the membrane will have a certain tension. If the balloon is now left to resume its natural spherical form, it will have a smaller surface and the tension on the rubber will be smaller. The surface layer of water, on the other hand, has the same tension whatever the form of the surface, and when a quantity of water of irregular shape becomes a spherical drop, there is not the slightest reduction of the surface tension in the process.

In the above explanation of the causes which produce surface tension, an assumption has been made which is not entirely correct, namely, that the particles in the surface are attracted only towards the interior of the liquid, and not at all towards the exterior. Strictly speaking, this can only be the case when the liquid surface is exposed to an empty space. If the surface is the region of contact with another substance, whether it be gaseous, liquid, or solid, the surface particles are attracted not only inwards, but also outwards by the molecules in the other phase, owing to the existence of a force of attraction between molecules of different kinds, which may be called adhesion. If the adhesion at a particular surface is equal to the cohesion the surface tension will be zero; but if the two forces have different values, the surface tension has a definite positive value which is different from (usually much less than) the value *in vacuo.* If the adhesion is less than the cohesion the surface film is compressed, owing to the attraction of the particles in the interior, while if the adhesion is greater it is compressed owing to the attraction of the particles of the other substance. According to these arguments the surface tension may have any value down to zero according to the nature of the phase with which the substance is in contact. It is also conceivable, and in fact it frequently happens, that the surface tension may be negative, *i.e.* the surface tends not to contract but to extend itself. On the mechanical grounds just outlined, this does not appear possible, and it is necessary to anticipate the explanation given in a later section, by stating that for a negative surface tension the surface must be electrically charged. When this is the case the charged particles repel each other and the surface seeks to expand. The expanding force thus produced opposes the contracting force due to the mechanical surface tension. If the electric charge is great and the mechanical tension is small, the former may predominate and produce a negative tension, causing the surface to become extended.

The simplest method of illustrating surface tension and of explaining its measurement is as follows.[1]

The wire DABC, bent twice at right angles, carries the wire DC in such a manner that the latter may move freely, either to or from AB with practically no friction. If a small quantity of liquid in the form of a thin film occupies the rectangle ABCD, the movable edge DC will tend to move towards AB, because the film of liquid on account of the tension in its two surfaces attempts to become as short and thick as possible. In order to retain the wire in the position DC a certain weight P must be attached to it. Experiment shows, moreover, that the weight is the same whatever the position of the wire DC, *e.g.* it is the same for DC as for D′C′. The weight is greater, however, the greater the length of DC, and is in fact directly proportional to the length. The surface tension of the liquid can accordingly be defined and measured as the pull exerted on the line DC. It must be particularly emphasised that the weight P is sustained only by the line DC, since the magnitude of the surface tension is sometimes wrongly associated with the area of the surface under consideration. The specific surface tension (or surface tension constant, or more briefly the surface tension of a liquid) is defined

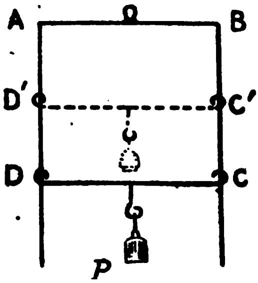

FIG. 1.

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[1] See, for example, Wiedemann and Ebert, *Physikalisches Praktikum* (Braunschweig, 1904), p. 130.

as the weight which is sustained by a line of 1 cm. length, or more generally as the pull which is exerted at right angles to its length and in the plane of the surface, by any line in the surface of 1 cm. length. In considering this force we are not restricted to straight lines only. Any irregular line exerts a pull which is proportional to its length. A circle of 1 cm. radius, chosen in any part of the surface, has an attraction for the neighbouring liquid particles equal to that of a straight line of length 2π cm.

The surface tension constant of a liquid depends on the nature of the liquid and on the temperature. The following table gives the constants for a number of the most important liquids.

TABLE I.

SURFACE TENSIONS OF SOME LIQUIDS AGAINST AIR IN DYNES PER CM.

	Temperature.	Method.	σ in $\frac{\text{dynes}}{\text{cm.}}$
Acetone	16·8°	Capillary	23·35
Ethyl ether	20°	„	16·49
„ „	40°	„	14·05
„ „	60°	„	11·80
„ „	80°	„	9·67
Ethyl alcohol	20°	„	22·03
„ „	40°	„	20·20
„ „	60°	„	18·43
„ „	80°	„	16·61
Benzene	17·5°	„	29·16
Chloral	19·4°	„	24·48
Chloroform	20°	„	25·88
Acetic acid	20°	„	23·46
Olive oil	20°	„	35·4
Cane sugar (molten)	160°	Drop	66·9
Water	0°	Capillary	75·49
„	10°	„	74·01
„	20°	„	72·53
„	30°	„	71·03
„	50°	„	67·8
„	80°	„	62·3

We have given above a clear definition of surface tension, and a method for measuring it. Experimental measurements by this method are, however, so difficult that it is not generally used for quantitative determinations.

In practice a number of different methods are used, of which a few will be outlined here without being described in detail.

The simplest process is the measurement of the height to which the liquid will rise in a capillary tube. If a glass tube of fine bore is dipped into water, the level of the water in the tube will rise above that of the water outside. The cause of the ascent is the property which water possesses of "wetting" glass. By this we mean that the water tends to spread itself as widely as possible over the surface of the glass. The reason for this will be discussed later (p. 33), but for the present the fact may be taken for granted. In consequence of the "wetting" a thin layer of water will rise on the walls of the tube. We can, therefore, represent this stage as in Fig. 2 ^{1}, where only the walls of the tube are covered with a thin film, the interior being free from water. The surface of the water in the tube is represented by ABCD. But in consequence of the surface tension this surface will tend to diminish and take up the form of Fig. 2 ^{2}, to accomplish which water must be raised. Since in the surface ABCD only the points A and D are fixed, we can consider the force which raises the water to be the pull which is exercised by the line of the circular circumference ADA on the rest of the water. As soon as the weight of water raised becomes equal to this point there can be no further ascent. Then the weight of the water raised is equal to the surface tension of the line ADA, i.e. to $2\pi r\sigma$, where r is the

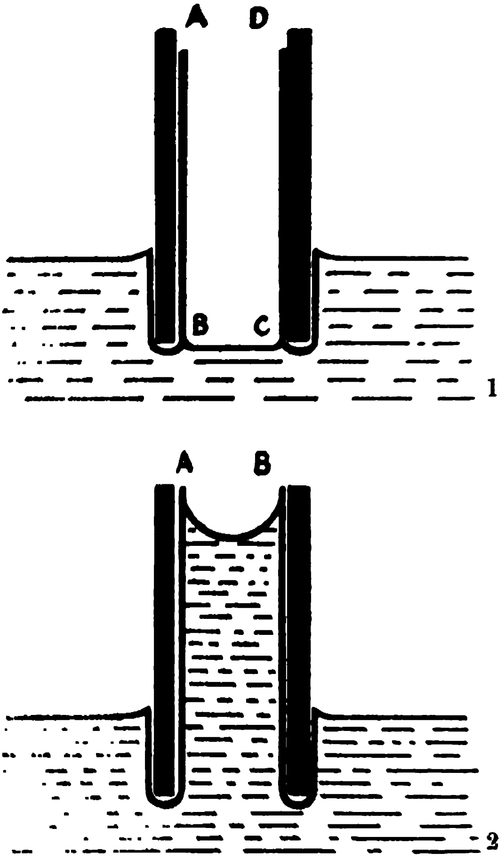

Fig. 2.

radius of the tube and σ the surface tension constant. The weight of the cylinder of water is $r^2\pi hs$, where h is the height of ascent and s the specific gravity of the liquid.

Then $$2\pi r\sigma = r^2\pi hs$$

and $$\sigma = \frac{rhs}{2}$$

that is to say, we can calculate the surface tension of the liquid from measurements of the radius of the tube, the specific gravity, and the height of the column of liquid. In this calculation it has been assumed that the "wetting" of the capillary by the liquid is complete, *i.e.* that the edge of the meniscus approaches the wall of the tube quite gradually (Fig. 3 left). According to G. Quincke, there is generally in practice a well-defined angle α between the direction of the meniscus and the wall of the tube (Fig. 3 right). The surface tension at the point A does not then act vertically upwards, and the weight of liquid raised is only counterpoised by the vertical component of the surface tension which is $\sigma \cos \alpha$. If $\alpha = 0$ as in the left-hand figure (perfect "wetting"), then $\cos \alpha = 1$. Otherwise the above formula becomes modified to

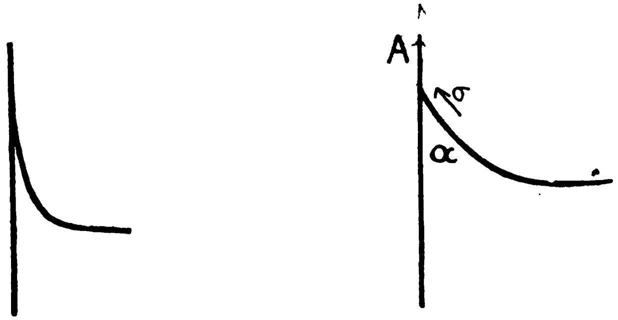

FIG. 3.

$$\sigma = \frac{rhs}{2 \cos \alpha}$$

A second method consists in measuring the size of the drops of the liquid when it flows from a narrow tube. If we consider water flowing out of a tube in a discontinuous manner with the formation of drops, we recognise that the drop is retained at the orifice by the tension in its surface. Only when the drop has grown so large that its weight is sufficient to overcome this tension is it possible for it to fall. The line of fracture of the surface is the line which has to support the greatest weight, *i.e.* the circle which marks the contact of the drop with the orifice. A very thin film of water will be retained on the glass walls of the orifice by an adhesive force which is greater than the surface tension. The falling drop does not break away from the glass tube itself, but from the adhering film of water. At the instant when the drop is detached the surface tension of the water in a line equal to the circumference of the orifice, is overcome by the weight of the drop, and therefore

$$\sigma 2\pi r = s$$

where s is the weight of the drop. This gives

$$\sigma = \frac{s}{2\pi r}$$

The weight of a falling drop can be obtained either by means of the balance, or by counting the number of drops which are formed by the flow of a known volume of the liquid from J. Traube's "stalagmometer." We need not discuss here the further complications of the theory of falling drops, since they do not lead to any conclusions valuable for our purpose.

Another good method, worked out by Whatmough, depends upon the measurement of the pressure which is necessary to expel bubbles of air from a narrow tube which dips into the liquid.

There are still many other methods for the measurement of surface tension which are described in textbooks of physics. Only the following two will be briefly outlined, since, as Freundlich has pointed out,[1] they have special features of some importance.

Dupré[2] measured the surface tension by means of the height of a stream of water forced upwards through a narrow opening, and Lord Rayleigh[3] determined it from the deformation which is produced in a stream of liquid flowing from an elliptical orifice. Such a stream assumes a circular cross-section at a little distance from the orifice, and a little further away again resumes its elliptical form with an exchange in the positions of the major and minor axis. The result is an oscillating stream with a definite frequency, and from the frequency it is possible to determine the surface tension.

The special characteristic of these methods is that the measurement is made upon a newly formed surface, whereas in the capillary method, the surface has reached a steady state when the measurement is made. For pure liquids this difference in the method of measurement does not lead to variable results, but in the case of many mixtures the surface tension diminishes when the liquid is allowed to stand for some time. The reason for this change will be explained later. In such cases the tension in the fresh surface is called dynamic, while the definitive tension in an old surface is described as static.

---

[1] H. Freundlich, *Die Adsorption in Lösungen*, Z. physik. Chem., 1907, **57**, 428, footnote.

[2] Dupré, *Travail et forces moleculaires*, II. Partie, p. 422. Quatr. procédé; Ecoulement, Ann. Chim. Phys., 1866, (4), **7**, 422.

[3] Lord Rayleigh, *On the Capillary Phenomena of Jets*, Proc. Roy. Soc., 1879, **29**, 71.

3. **Surface Energy.**—If we describe surface tension as a force, it follows that work can be performed by its operation. Where a surface disappears o diminishes, the force is available for the production o work, and where new surface is formed work must b done against the force. The more the surface extended the more work must be done. Since we hav seen, however, that the surface tension constant is ind pendent of the extent of the surface, it is necessary t introduce the area as a second factor in the determination of the power of the surface to do work. Th power to do work we call energy, and in the measurement of surface energy we must, as Ostwald has demonstrated, consider the surface tension together with the area of the surface. When either of these factors is zero then the surface energy is zero. Consequently the surface energy may be taken as the product of the two quantities, just as all other forms of energy are measured as products. For example, electrical energy is the product of a quantity of electricity into a difference of potential, volume energy is the product of a pressure into a change of volume, and so on. Surface energy, then, is the product of the surface area into surface tension

$$\Omega = \omega . \sigma$$

Here Ω is the surface energy, ω the surface, and σ the surface tension constant.

The two factors, whose product represents a quantity of energy, can usually be clearly differentiated. One factor may be represented as a "force," the other is always the measure of some quantity such as expansion, size, volume, surface area, etc. Ostwald has very conveniently called the first factor the "intensity factor" and the second the "capacity factor." If different parts of a system exhibit differences in regard to the intensity factor of any form of energy, there will always be a tendency to equalisation. The intensity factor of heat, for instance, is temperature, and differences of temperature always tend to disappear. On the other hand, there is no tendency towards the equalisation of differences in capacity factors. If two bodies have the same temperature but different capacities for heat, they may be placed in contact without any transfer of heat taking place. In the case of surface energy the surface tension is apparently, at first sight, the intensity factor, and the size of the surface the capacity factor. If there is in an isolated system any inequality in the intensity factor of surface energy, the inequality should tend to disappear. In all systems, of course, the surface tension is found only in the surface, its value in the interior of the liquid being zero. Therefore the surface tension will always tend to diminish as far as possible. In the case of a chemically pure liquid, there is no possibility of any change which will reduce the surface tension below the characteristic value for that liquid. We shall, however, shortly meet with other cases where changes can take place which result in a reduction surface tension. Now experience shows that the other factor of surface energy, namely the area of the surface, always tends to become reduced to a minimum value. An explanation of this behaviour on the basis of the molecular hypothesis has already been given. We can, in other words, represent the area of the surface as an intensity factor, and we must therefore conclude that the resolution of surface energy into intensity an capacity factors is somewhat ambiguous. The syste of Ostwald cannot be applied in this case withou confusion. The one definite conclusion which can b stated is that surface energy tends to diminish as far a possible in all cases by all conceivable means. This fundamental principle accounts for numerous important changes, not only of form and shape, but also of chemical constitution in the living organism. The quantities of energy which are located in surfaces are not at first sight of remarkable magnitude. The production of a water surface of 1 sq. cm. requires an expenditure of only 70 ergs $= 7 \times 10^{-7}$ kg. meters $= 1{\cdot}7 \times 10^{-6}$ small calories. Notwithstanding this, one of the factors of surface energy, viz. the area of the surface, has such an enormous value in living organisms, that living matter must have a remarkably large amount of energy accumulated as surface energy.

According to the above principles the effects of surface energy can be divided into two groups, first those produced by the tendency of the surface tension to diminish, and second those produced by the tendency of the area of the surface to diminish as far as possible.

The first principle will be referred to as that of the maximum reduction of surface tension, the second as the principle of maximum surface contraction.

4. Surface Contraction.—The principle of maximum surface contraction may be illustrated in the simplest manner if we consider a fixed quantity of liquid, which for some reason or other has assumed a form which does not satisfy the condition of minimum surface. For example, if two non-miscible liquids have been divided by shaking into a system of drops, the drops, if left to themselves, will gradually aggregate into larger ones. The final form in the absence of gravity would be a single large sphere, but under the action of gravity the liquids become separated by a horizontal surface.

This simple process, however, only takes place in the case of perfect liquids which have no form-elasticity, *i.e.* which offer no resistance to a change of shape. If we have an imperfect liquid, more or less jelly like, possessing a certain amount of form-elasticity, distributed in small drops throughout a liquid phase, then the action of surface tension in causing the union of small drops to larger ones is subject to limitations. For instance, two small globules of a jelly-like substance, suspended in a perfect liquid, may as a result of their motion come into contact with each other, and then, under the influence of surface tension, they will tend to unite, forming first a dumb-bell shaped mass, and finally, by the steps indicated in the figure, a single sphere. How far this process will continue depends on the elasticity of the liquid.

No further change will take place when the tendency of the elasticity to resist the change of shape is equal to the tendency of the surface tension to reduce the surface area to a minimum. In biology it is frequently necessary to consider cases in which semi-liquid systems of relatively great form-elasticity come into contact. In such cases an appreciable change in the surface is not possible on account of the great resistance offered by the elasticity. The change proceeds further, however, in either of the following contingencies: (*a*) if from any chemical or physical cause the consistency of the particles changes in such a way that the elasticity is diminished (*e.g.* by a change from a stiff to a sticky jelly); or (*b*) if for any reason the surface tension at the boundary between the two phases is increased (*e.g.* by a diminution in the electrical potential of the surface). The two conditions may of course act in conjunction with each other.

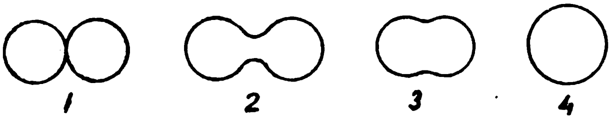

FIG. 4.

The action of surface tension on gelatinous substances is therefore to promote the union of previously separated particles. When it brings about the union of coarsely microscopic particles to macroscopic lumps, this action is called agglutination, an expression which finds special use in connection with the aggregation of cellular elements. When the action causes the union of finely microscopic or ultra-microscopic particles it is called flocculation or coagulation. From what has been said above it follows that the agglutination and coagulation are produced when either the surface tension has a specially high value, or the opposing elasticity is very low.

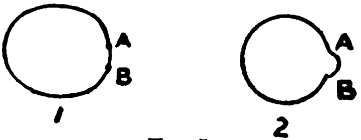

FIG. 5.

Up to this point we have assumed that the surface tension of a particle is uniform over its whole surface, which is always the case for a single liquid. In structures such as living cells, however, which consist of complicated mixtures of different substances, sudden differences of surface tension between different parts of the surface may arise, caused by local changes of composition under the action of stimuli. If the surface tension in the circumference of the circular cross-section of the cell (see Fig. 5) suddenly increases in one portion AB, the sphere will tend to become flattened in this neighbourhood. If the surface tension at AB suddenly diminishes, then the shape will change as in Fig. 5 (2). Generally speaking, the total surface energy has a minimum value, *e.g.* if σ is the surface tension, and ω the area of one of the sections, and σ' the surface tension, and ω' the area of the other section, then the surface energy

$$\Omega = \omega\sigma + \omega'\sigma'$$

will reach a minimum value, owing to the progress of changes in ω and ω'. The portion of the surface in which the tension is greatest will become as small as the conditions allow, and the other portion will become correspondingly great. This is obviously the mechanism of the amœboid movement of protoplasm; the local changes of surface tension are probably caused by the presence of products of local fermentative processes taking place under the action of stimuli. The principle of surface contraction also explains why many substances move rapidly to and fro in variou directions when they are placed on the surface o water. A well-known substance which exhibits thi property is camphor, and others are glacial acetic acid phenol, benzoic acid, potassium, calcium, and magnesium butyrates, etc. When the motion has persisted for a little while it ceases completely, while if the water is previously saturated with the substance under observation no motion takes place at all. The explanation depends on the fact that a solution of camphor has a lower surface tension than pure water. When a piece of camphor comes into contact with water it becomes surrounded by a layer of saturated solution. The difference in surface tension between this layer and the rest of the water is the cause of disturbances in the surface which result in the motion of the particles of camphor. As soon as the solution becomes saturated the surface tension is everywhere the same, and no further disturbances can be produced.

5. **The reduction of Surface Tension. Mechanical Adsorption.**—In a chemically pure liquid there is no possibility of a reduction of surface tension, and so long as the area of the surface remains unchanged no work can be done by the surface tension.

When the liquid is a mixture of several chemical individuals the state of affairs is different. For example, the surface tension of acetic acid is less than that of water, and the values for mixtures of these two substances are intermediate between those for the pure liquids.

TABLE II.

INFLUENCE OF SOME SUBSTANCES ON THE SURFACE TENSION OF WATER.

(The surface tension of pure water is taken as unity.)

Concentration of solution per cent. by volume of	Methyl alcohol.	Ethyl alcohol.	Iso-propyl alcohol.	Isobutyl alcohol.	Amyl alcohol.	Capryl alcohol.
0·0	1·000	1·000	1·000	1·000	1·000	1·000
0·05						0·638
0·4				0·866		(0·10%) 0·521
1·0	0·962	0·933		0·742	0·594	(0·16%) 0·444
2·0				0·640		
5·0	0·856	0·785	0·680	(4%) 0·525	(4%) 0·358	
10	0·777	0·682	0·574			
20	0·660	0·568				
30	0·590	0·490	0·395			
60	0·458	0·382	0·330			
80	0·392	0·350				
100	0·302	0·302	0·300			

[See Duclaux, *Ann. Chim. Phys.*, 1878, **13**, 76.]

Per cent. by volume.	Acetic acid.	Butyric acid.
0·5		0·838
1	0·940	0·752
2	0·901	0·655
5	0·819	0·51
10	0·741	0·41
20	0·644	
50	0·514	
100	0·396	

Although it has not yet been found possible to represent the surface tension as a function of the concentration, its value becomes gradually smaller as the percentage of acetic acid is increased. Consequently, a reduction of surface tension may be produced if the surface becomes richer in acetic acid than the rest of the liquid. This was first pointed out by Willard Gibbs[1] and J. J. Thomson,[2] and the idea has been further developed by H. Freundlich.[3]

We may, therefore, say that the surface tension exerts an attraction on the dissolved substance tending to draw it into the surface. The greatest conceivable reduction of surface tension would be reached when the surface layer was composed of pure acetic acid and all the water was in the interior of the liquid, but such a state of affairs cannot be attained on account of the opposition of osmotic forces. When a solution has its dissolved substance in different concentrations at different points the concentrations tend to become equalised by diffusion. An adsorption equilibrium is therefore produced in which the attraction of the acetic acid towards the surface due to the surface tension is equal to the opposed osmotic force. The analytical determination of this equilibrium may be attempted in the following manner, which differs somewhat from the method of Gibbs. Assuming that equilibrium has been established, let the surface tension be σ, the concentration of the solution c, and that of the surface layer C. Suppose now that the equilibrium is slightly disturbed by the passage of a very small quantity dx of adsorbable material into the surface, so that the surface tension falls by an amount $d\sigma$. In this way, if the area of the surface be ω, the amount of work obtained from the change in the surface energy is $\omega d\sigma$. The osmotic work obtained from the diffusion process is $dx\mathrm{RT}\log\frac{\mathrm{C}}{c}$. (When one gram molecule of a substance is removed from a place where it is under the pressure P to a place where it is under the pressure p, the work done is $\mathrm{RT}\log\frac{\mathrm{P}}{p}$, and since the ratio of osmotic pressures, at least in dilute solutions, is equal to the ratio of concentrations, this becomes $\mathrm{RT}\log\frac{\mathrm{C}}{c}$ Therefore, when dx gram molecules are transported, the work done is $dx\mathrm{RT}\log\frac{\mathrm{C}}{c}$.)

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[1] J. Willard Gibbs, *Scientific Papers* (London, 1906), Vol. I, p. 240.

[2] J. J. Thomson, *Application of Dynamics to Physics and Chemistry*, London, 1888.

[3] H. Freundlich, *Die Adsorption in Losungen*, Z. Physikal. Chem., 1907, 57, 385.

Now it is a characteristic of equilibrium that the algebraic sum of the various forms of energy produced by a small disturbance shall be zero. Therefore

$$\omega d\sigma + dx\mathrm{RT}\log\frac{\mathrm{C}}{c} = 0$$

C may be written $= \frac{x}{\mathrm{V}}$, where V is the volume of the surface film, and x the quantity of dissolved substance contained in it. Consequently

$$dx = \mathrm{V}d\mathrm{C}$$

and $$\omega d\sigma + \mathrm{V}\,.\,d\mathrm{C}\,.\,\mathrm{RT}\log\frac{\mathrm{C}}{c} = 0$$

or $$\log \frac{C}{c} = -\frac{\omega}{V.RT}\frac{d\sigma}{dC}$$

$\frac{V}{\omega}$ is the volume of the surface layer divided by th area of the surface. If we assume the surface layer t be an extended thin parallelepiped, then $\frac{V}{\omega} = \delta$, th thickness of the layer, and

$$\log \frac{C}{c} = -\frac{1}{\delta.RT}\frac{d\sigma}{dC}$$

or $$C = c.e^{-\frac{1}{\delta.RT}\frac{d\sigma}{dC}}$$

Let us consider the meaning of the different members of this equation. C, the concentration of the adsorbed material, is not capable of experimental determination, but assuming that the thickness of the surface layer is practically uniform, the quantity of adsorbable material taken up by a given weight of adsorbent is at any rate proportional to C. The concentration of the solution c is easily determined. The thickness of the adsorption layer δ cannot be determined directly, but we shall obtain a similar expression later in considering the kinetics of surface reactions, and perhaps we may assume by analogy with that case that δ is equal to a few hundredths of a millimetre, and diminishes as the temperature rises. R is the gas constant and T the absolute temperature.

$\frac{d\sigma}{dC}$ represents the influence of the dissolved substance in reducing the surface tension. It expresses as a differential quotient the variation of the surface tension with the concentration of dissolved substance in the surface layer and may be called the "surface tension reducing capacity" of the solute.

In the above reasoning it has been assumed provisionally, that the surface layer is sharply defined from the rest of the liquid. This, of course, is not actually the case, and the transition, though rapid, is gradual, so that we get a corresponding continuous fall in concentration from the surface to the interior of the solution. Experimentally it is only possible to determine the total quantity of substance adsorbed, and not its concentration in the surface. The area of the adsorbing surface is also incapable of measurement if such adsorbents as powdered charcoal are used in order to get better effects. In such cases we only know that the surface is proportional to the quantity of charcoal used, provided the latter is of a uniform degree of subdivision, and is well mixed before use.

In spite of these theoretical deficiencies we can deduce from the formula certain facts which agree with experience. The quantity of material adsorbed increases with the concentration of the unadsorbed material, *i.e.* the amount of adsorption increases as more substance is added, but there is no proportionality. Adsorption is always less at higher temperatures, and it is greatest for the substances which produce the greatest lowering of surface tension.

Now it is obvious that a substance can only lower the surface tension when this has an original value greater than zero. $\frac{d\sigma}{dc}$ is a function of σ and $= 0$ when

$\sigma = 0$, that is to say, adsorption can only take place a surfaces which have a positive surface tension. If an substance which is known to lower the surface tensio at a water-air surface is not adsorbed from water b kaolin, we can conclude that the surface tension at water-kaolin surface is zero, and further that no othe substance will be *mechanically* adsorbed by kaolin. These conclusions are confirmed by experiment. The absence of surface tension between the two phases indicates, according to our previous argument (p. 8), that the cohesion of water is practically identical with its adhesion to the other phase.[1]

As a matter of fact a number of substances are adsorbed by kaolin, but we shall see later (p. 82) that this is a phenomenon entirely different from the mechanical adsorption we have just been studying.

There is as yet no direct method available for the measurement of the surface tension at a liquid-solid surface, but we can nevertheless draw certain conclusions with regard to its limiting value from the extent of the adsorption by the solid of material dissolved in the liquid.

We have only dealt hitherto with those solutes which lower the surface tension of the solvent. There are, however, also cases in which the surface tension is raised. In such cases the adsorption will be negative, *i.e.* the concentration of the adsorption layer will be lower than that of the rest of the solution.

When a new surface is produced in a solution, *e.g.*

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[1] We must here include under cohesion and adhesion the sum of all attracting and repelling forces between the molecules, both mechanical and electrical.

y shaking, the concentration of the solute is at first niform in the whole solution, including the surface, nd the surface tension has the definite value required y this concentration. Very soon, however, there is a passage of solute into the surface layer due to adsorption, accompanied by a diminution in surface tension. Therefore the surface tension of a new surface soon changes and different values are obtained by different methods according as they use fresh or old surfaces. The surface tension in the condition of equilibrium is static and may be measured by the capillary method. The surface tension of a new surface is dynamic and may be measured by the above-mentioned methods of Dupré and Rayleigh (p. 15).

The substances, which in quite small concentrations distinctly lower the dynamic surface tension, are much more numerous than those which raise it. The reason for this important fact is given by Gibbs (*loc. cit.*) as follows. A substance which lowers the surface tension is adsorbed by the surface, and since it is the concentration at the surface which determines the change in surface tension, the adsorption brings about a further accentuated diminution. Solutions of such substances with quite minute total concentrations, have surface layers in which the concentration is relatively high. Conversely, when a substance raises the surface tension it is negatively adsorbed, and consequently the surface has a lower concentration than the bulk of the solution. As a result the influence of the substance on the surface tension is only exhibited to a relatively small extent.

It is found in practice that certain substances which have only a small influence (certainly not a lowering influence) on the surface tension of water are nevertheless adsorbed to a slight extent. To this class belong the various sugars.[1] According to the above formula (p. 26),

$$\text{when} \quad \frac{d\sigma}{dC} = 0 \quad \text{then} \quad C = ce^0 \quad \text{or} \quad C = c$$

i.e. there should be no adsorption. It is necessary, therefore, to find some explanation on other grounds. The solubility of a substance is known to depend to some extent on the external pressure; if there is a contraction on solution, then an increase of pressure increases the solubility, and *vice versâ*. It is therefore quite conceivable that a solute which has no effect on the surface tension, will divide itself between the surface layer and the rest of the solution according to the partition coefficient which regulates its solubility under the differing pressures which prevail in the surface and in the solution. Under these conditions, in dilute solutions

$$C = kc$$

where k is the partition coefficient. This formula does not agree very well with the results of experiment in the case of the sugars; but it must be remembered that the concentration of the surface layer, if adsorption can actually be detected, must be very much greater than that in the solution. Consequently, even when the bulk of the solution is very dilute the surface layer is so concentrated that the laws of dilute solutions are no longer valid. The experiments might be repeated with advantage in more dilute solutions than those hitherto used, in order to decide whether the results agree approximately with the above formula.

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[1] Rona and Michaelis, *Biochem. Zeits.*, 1909, **16**, 489; Adler and Herzog, *Kolloid.-Zeits.*, 1908, **2**, Suppl. Heft II.; Herzog, *Z. Physiol. Chem.*, 1908, **60**, 79.

In future it will be convenient, for the sake of brevity, to make use of the following expressions. A substance which leaves the surface tension of water unchanged will be known as "homoiotonic," and one which changes it as "allotonic." Those allotonic substances which lower the surface tension will be called "bathotonic," and those which raise it "hypsotonic." Mechanical adsorption will then be a general property of bathotonic substances, and will be exhibited in exceptional cases by homoiotonic substances.

6. **Adsorption of Mixtures.**—Up to this point we have only studied the case of adsorption from a solution containing a single dissolved substance. In biological processes this condition is scarcely ever fulfilled, and we are usually concerned with mixtures. If all the dissolved substances are bathotonic, they will all contribute to the lowering of the surface tension. If a bathotonic and a homoiotonic substance are present together, the presence of the latter will not interfere with the adsorption of the former, so long as it does not interfere with its effect on the surface tension. This condition will be approximately fulfilled when only dilute solutions are considered.

When two bathotonic substances are present in a solution, their mutual influence with regard to adsorption may be explained by the following example.[1]

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[1] L. Michaelis and P. Rona, *Untersuchungen über Adsorption*, Biochem. Zeitschrift, 1909, 15, 196. Masius, *Dissertation*, Leipzig, 1909.

If acetic acid and animal charcoal are both added to an aqueous solution of acetone, acetic acid will be adsorbed at the charcoal surface because it lowers the surface tension. We may take it for granted that the "surface-tension-lowering influence" of the acetic acid will be greater for pure water than for water which has already had its surface tension reduced by the addition of acetone, *i.e.* $\frac{d\sigma}{dc}$ is greater the greater the value of σ.

Acetic acid will, therefore, be more strongly adsorbed from a pure aqueous solution than from a solution which also contains acetone, and, in general, each of two adsorbable substances will displace the other to some extent from the adsorption layer. The displacing power is in fact subject to the same rules as the adsorption itself. One substance displaces another to a greater extent, as the concentration of the displacing substance is increased, but the effect increases more slowly with the concentration when the concentration itself is higher. The more a substance lowers the surface tension of the solvent, the more it will displace another substance from the surface layer of that solvent. Substances which are not themselves adsorbed have little or no effect on the adsorption of others. Those substances which are strongly adsorbed even from quite dilute solutions, are most susceptible to displacement by others.

This mutual displacing effect during adsorption is found not only among bathotonic substances, but also among the few existing adsorbable homoiotonic substances such as the sugars. The sugars are displaced from the adsorption layer by other mechanically adsorbable substances, though attempts to explain the displacement are met with the same difficulties as the attempts to explain the adsorption itself (p. 30).

7. **Anomalous Adsorption and the Formation of Surface Membranes.**—In certain cases the process of adsorption has a very important consequence. If the dissolved adsorbable material increases the internal friction (*i.e.* the viscosity) of the solvent, the accumulation of this material in the surface layer will give the layer a viscous consistency, and so increase its mechanical rigidity. In this way comparatively strong, unbreakable membranes may be formed at the surface.[1] Albumen, the albumoses, saponin, many colouring matters and soaps, are all examples of substances which fulfil the conditions necessary for the production of a surface membrane, *i.e.* they lower the surface tension and greatly increase the viscosity of water.

Such membranes are sometimes formed in circumstances in which they have an important bearing on the stability of emulsions. When a drop of oil is placed on the surface of water, the system has at first three boundary surfaces, water-air, water-oil, and oil-air. But the sum of the tensions in the oil-air and water-oil surfaces is less than that in the water-air surface. The principle of maximum reduction of surface tension consequently requires that the oil shall spread itself over the surface of the water so that the water-air boundary completely disappears.[1]

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[1] Ramsden, *Z. physikal. Chem.* (1904), **47**, 342. M. V. Metcalf, *Z. physikal. Chem.* (1905), **52**, 1. H. Zangger, *Vierteljahrsschr. naturforsch. Ges.*, Zurich, 1908, **53**, 408.

The spreading is, therefore, as great as possible even with very small quantities of oil, since a reduction of surface tension is achieved, when the oil-film is only a single layer of molecules. In living cells oily substances are always present in considerable quantity, not as in the foregoing example in coherent masses of considerable size, but in the finest suspension, or what is usually called colloidal solution. The droplets of oil are at first almost uniformly distributed throughout the cell, but some of them tend, in consequence of the Brownian movement and other impulses, to find their way to the surface. When this happens the drop immediately spreads itself as a very thin coating on the surface of the cell.

Such a heterogeneous system consisting of two liquids either totally or nearly immiscible has, however, a particularly important function in the construction of the cell. When a very finely divided substance corresponding to the oil is present in another medium, there are certain conditions in which the droplets cannot aggregate into larger drops, and a permanent suspension or colloidal solution is formed. The essential condition is that the surface tension between the aqueous solution and the oil drops shall be, for some reason or other, practically zero. If we assume electrical disturbances to be absent, this is the case when a strongly bathotonic substance, such as soap, is present in the aqueous solution. In the case of an oil-water system there is always a possibility of the formation of a small quantity of soap, particularly when the water is alkaline. The oil always contains a little free fatty acid, and the alkali would also very soon have a saponifying effect. The soap reduces the surface tension, and is, consequently, strongly adsorbed. The effect of the adsorption is to cause still further reduction in the surface tension, and, consequently, a greatly diminished tendency for the oil drops to flow together. If the surface layer is made more viscous by the adsorbed material, the conditions for the stability of the emulsion are entirely fulfilled.

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[1] G. Quincke, *Pogg. Ann.* (1870), **139**, 80.

As a general rule, therefore, a permanent suspension of a liquid which is not soluble in water may be obtained by adding to the water a bathotonic substance, *i.e.* one which is adsorbed by the surface of separation of the two liquids. This emulsifying power, however, is not possessed by all bathotonic substances, but only by those which raise the viscosity of the water to produce surface layers of marked rigidity. Too little importance is often attached to this limitation, but substances like alcohol, acetone, and ether which, although they lower the surface tension also lower the viscosity, cannot have an emulsifying effect because the absorption septa are too easily fractured. On the contrary, an extremely bathotonic substance like ether will cause most foams to subside, since it displaces from the adsorption layer a considerable quantity of the material which is responsible for the rigidity of the film.[1]

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[1] A foam is analogous to an emulsion, being a suspension of a gas in a liquid, while an emulsion is a fine suspension of a liquid in a liquid.

The following are bathotonic substances which increase the viscosity of water :—soap, saponin, salts of the bile acids, gum-arabic, gelatine, albumen, and the albumoses. They are, therefore, used as emulsifying agents and their aqueous solutions will yield lasting foams when shaken. The membrane formation in solutions of such substances is easily recognised under varying conditions and often without any special manipulation, since a solid layer of considerable mechanical rigidity separates at the surface on standing, even when evaporation is prevented. Metcalf[1] has made direct measurements of the strength of such surface membranes. The phenomenon of membrane formation is responsible for a very important complication in the surface conditions. In the case of liquids of low viscosity the whole of the rigidity of the surface, which requires, for instance, that a drop of liquid flowing from a tube shall attain a certain definite weight before it falls, is caused by the surface tension. Where a surface membrane has been formed, however, the rigidity is due not only to the surface tension, but also, and often to a much greater extent, to the mechanical strength of the membrane. If, for example, a quantity of soap solution is introduced into the framework described on p. 9, and the weight attached, the measurement made includes not only that of the true strength of the surface, *i.e.* surface tension, but also the rigidity of the soap membrane which is formed at the surface. Consequently, with such substances it is found that capillary phenomena are fundamentally modified. If a solution of albumen, for instance, is allowed to rise in a capillary, it is found after a time that within comparatively wide limits, its meniscus will maintain any position into which it is brought, or at any rate that it will only very slowly take up the true position demanded by the surface tension; it behaves as if the solution adhered with some tenacity to the wall of the capillary. Since we are almost exclusively concerned in living organisms, with such albuminoid solutions, it follows that the laws of capillarity in the organism are very widely different from those in less viscous fluids, a fact which is not as yet properly appreciated.

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[1] Metcalf, *Z. physik. Chem.*, 1905, **52**, 1. References to other literature are given.

Substances of this group have a second special characteristic. While with all "normally adsorbable" substances the process of adsorption is a perfectly reversible one, the adsorption of substances like albumen, the albumoses, dyestuffs, and soaps, is entirely, or almost entirely, irreversible. When charcoal, laden with adsorbed albumen, etc., is washed with water, the adsorbed material does not go back into solution to any appreciable extent, as demanded by the new conditions. In explanation of this phenomenon it is only possible to offer opinions, but perhaps the following preliminary suggestions may be put forward. If an ordinary, readily diffusing, substance is dissolved in water and the solution shaken with charcoal, then the equilibrium difference of concentration between the surface layer and the body of the solution which is demanded by the laws of adsorption, is more rapidly attained than it would be if mere diffusion were at work. A thin layer of water, however, adheres so closely to the charcoal that it moves with the charcoal particles and is not disturbed by the shaking. We shall return to the consideration of such adhesion layers later (p. 108). The transport of dissolved substance through the stationary layer is not assisted to any extent by shaking, and this portion of the process which is necessary for the attainment of equilibrium, depends entirely on pure diffusion. Hence if we are dealing with substances which only diffuse extremely slowly, the ready attainment of equilibrium is rendered very difficult by the slowness of the diffusion process. We know, however, that the equilibrium is easily reached from one side, *i.e.* by the progress of adsorption, while the process is not accelerated in the direction of the solution of previously adsorbed material. It appears, therefore, as if it were possible by shaking to accelerate the movement of feebly diffusing material towards the carbon surface, but not the movement away from the carbon surface. It is not yet possible, however, to account in any way for this conjectured behaviour.

There is also a third quite puzzling phenomenon amongst this group of substances. We have seen that when two adsorbable substances are present together, each reduces the adsorption of the other. This law only holds for normal adsorption. When a normal and an anomalous substance are present together, the one has no effect on the adsorption of the other. It has been proved, for example, that the adsorption of acetone (a typical bathotonic substance), or that of sugar (a typical adsorbable homoiotonic substance), is in no way affected by albumen, albumoses, or, so far as has been investigated, by dyestuffs.[1]

This phenomenon may be described as the non-validity of the law of displacement for mixtures of simple crystalloidal substances with colloidal or highly viscous substances which are subject to "anomalous adsorption."

Although high viscosity, feeble diffusing power, and colloidal character of the solution are all to some extent involved together in anomalous adsorption, it must not be assumed that all these properties have the same significance. Uncertainty in this respect is due to the fact that it is not yet decided which of these properties is primarily responsible for the special position with regard to adsorption. All such substances investigated up to now have all three properties. The circumstance that sugar which is normally and reversibly adsorbed, has a considerable effect on the viscosity of water, but diffuses readily, is evidence for the view that anomalous adsorption is principally due to feeble diffusive power.

Finally, substances which are anomalously adsorbed show a fourth characteristic. The adsorption of normal substances depends on the concentration of the substance in the surrounding solution, but that of anomalous substances depends almost entirely upon the absolute quantity present. For example, 1 grm. of charcoal will adsorb a greater portion of 1 grm. of acetone when the amount of solvent (water) is diminished. In the adsorption of 1 grm. of albumose by 1 grm. of charcoal it is practically of no importance, how much water is used to dissolve the albumose.

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[1] Masius, *loc. cit.* Masius does not give this explanation of his experiments.

8. **The (Empirical) Formulæ for Adsorption Equilibrium.**—There are two empirical formulæ which represent the equilibrium between adsorbed and dissolved material in a satisfactory manner. The older expression due to Küster,[1] Schmidt,[2] Appleyard and Walker,[3] and W. Biltz,[4] is

$$(1) \qquad \frac{x}{m} = k\left(\frac{a-x}{v}\right)^{\frac{1}{p}}$$

$$\text{or } (2) \qquad C_1 = kC_2^{\frac{1}{p}}$$

where a is the total quantity of adsorbable material, x the adsorbed quantity, m the quantity of adsorbent (which may be taken as proportional to the adsorbing surface), and v the volume of the solution; $\frac{x}{m}$ is consequently the "concentration" of the adsorbed substance in the adsorbent ($= C_1$), and $\frac{a-x}{v}$ the concentration of the unadsorbed portion in the solvent ($= C_2$). The actual value of the constant k has not yet been determined with accuracy, since it is not possible to measure the surface of a finely divided substance. Comparative values can, however, be obtained by using adsorbent from the same source and in the same state of subdivision. The value of the exponent is definite and characteristic for each substance and varies only with the temperature. Its significance, however, is not at all clear.

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[1] Kuster, *Z. physik. Chem.*, 1894, **13**, 445.

[2] G. C. Schmidt, *Z. physik. Chem.*, 1894, **15**, 56.

[3] Appleyard and Walker, *J. C. S.*, 1896, **69**, 1334.

[4] W. Biltz, *Ber*, 1904, **37**, 3138.

The value $\frac{1}{p}$ is usually about 0·5, although it is sometimes as low as 0·2 or as high as 0·8. In a very large number of cases the deviations from 0·5 are so small, that it is a matter for doubt whether the exponent is not always 0·5 within the limits of experimental error.

A formula such as the above, especially one with an exponent which is an integral or a simple fraction, is very similar to those which are derived from the law of mass action or from Henry's partition law. The second of these laws in particular seems to offer some information on the nature of the process, and suggests a closer comparison. If a substance is divided between two solvents, and its molecular weight in one solvent is n times, and in the other m times the smallest molecular weight conceivable on theoretical grounds, then Henry's partition law applies as amplified by Nernst, *i.e.*

$$\frac{C_1^{\frac{1}{n}}}{C_2^{\frac{1}{m}}} = \text{constant}$$

or

$$\frac{C_1}{C_2^{\frac{n}{m}}} = \text{constant}$$

If the adsorbing material is looked upon as a solid solvent, we can attempt to represent the adsorption law as a simple partition law between two solvents

$\frac{x}{m}$ is then C_1, $\frac{a-x}{v}$ is C_2, and $kC_1 = C_2^{\frac{n}{m}}$. If $\frac{n}{m} =$ about 0·5, as is frequently the case, it follows that the adsorbed substance has twice as great a molecular weight in water as in the adsorbent. This is, however, in many cases inconceivable. In the case of acetone, for example, the law would imply that its molecular weight in water was twice as great as in solid solution in the charcoal. But acetone dissolved in water has been proved to have the smallest conceivable molecular weight, and not to be associated to form double molecules. It is apparent, therefore, that the agreement between the adsorption formula and the partition law is only accidental. We cannot deduce from it a theory of adsorption as a process of solid solution in the adsorbent; in fact, it is directly opposed to such a theory.

When we attempt to decide in what way the "adsorbability" of a substance must be defined, we are led to the conclusion that for its definition two constants are always necessary. Since the constant $\frac{1}{p}$ is in general not very different from 0·5, the adsorbability may be defined approximately as the value of k in the above equation. The action of equal numbers of molecules of different adsorbable substances in lowering the surface tension is indicated by the value of k, while the exponent $\frac{1}{p}$ is connected with the relation of this lowering of surface tension to an increasing concentration of the substance.

The second formula for the adsorption equilibrium, due to Freundlich,[1] is to some extent rational. Freundlich found the relation between quantity of charcoal and adsorption empirically in the following manner. If a system consisting of charcoal and solution already in equilibrium is taken, and a little more charcoal is added to it, but no more dissolved substance, then further adsorption takes place, the quantity adsorbed being proportional to the concentration of the non-adsorbed substance in solution.

$$\frac{dx}{dm} = \lambda \frac{a-x}{v}$$

From this we obtain by integration

$$\frac{v}{m} \log \frac{a}{a-x} = \lambda$$

Of course it is not possible to say anything *à priori* with regard to the significance of λ. It appears empirically that it is proportional to a negative fractional power of the concentration before adsorption

$$\lambda = \alpha\left(\frac{a}{v}\right)^{-\frac{1}{n}}$$

when α is the proportionality factor, $-\frac{1}{n}$ the exponent.

The adsorption equilibrium is therefore given by

$$\frac{v}{m} \log \frac{a}{a-x} = \alpha\left(\frac{v}{a}\right)^{-\frac{1}{n}}$$

In order to bring the two apparently different formulæ into agreement Freundlich expanded the exponential portion of his formula by means of the binomial theorem, and the logarithmic portion by means of Taylor's theorem. Neglecting the higher members of the series, and assuming that $\frac{1}{p} = \frac{1}{2}$, the other formula can then be deduced from the Freundlich expression. Since $\frac{1}{p}$ is usually about $\frac{1}{2}$, both formulæ are found to agree satisfactorily with the facts. The logarithmic expression of the older formula is

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[1] H. Freundlich, *loc. cit.*

$$\log C_1 = \frac{1}{p} \log C_2 + \log k$$

and that of the Freundlich formula

$$\log \lambda = -\frac{1}{n} \log \frac{a}{v} + \log a$$

These two equations both represent straight lines, being of the type

$$y = ax + b$$

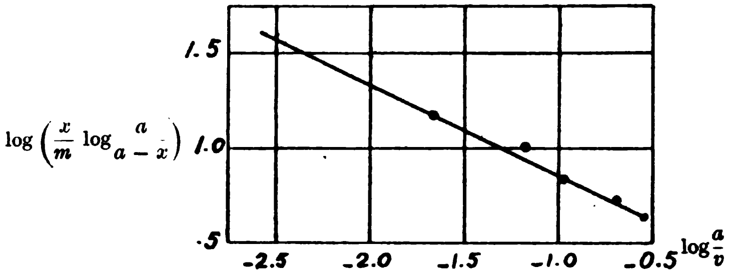

FIG. 6.

The straight line corresponding to the Freundlich equation (Fig. 6) falls obliquely to the axis of x, the other one (Fig. 7) rises when similarly plotted. The angles of inclination of the two lines are together equal to 90°, the tangents being the characteristic exponents $\frac{1}{n}$ and $\frac{1}{p}$

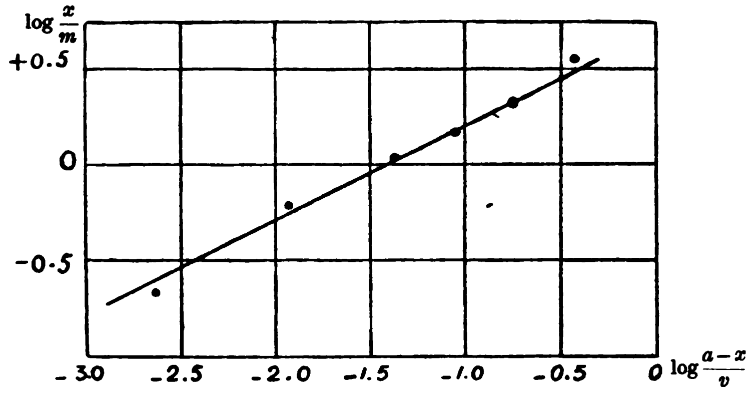

FIG. 7.

It was mentioned above that in the case of anomalous adsorption the volume of the solvent has often no influence on the degree of adsorption. This means that in the older formula the exponent is zero,

$$\frac{x}{m} = k\left(\frac{a-x}{v}\right)^0$$

$$i.e. \frac{x}{m} = k.$$

The volume thus disappears from the equation, and with it the total amount (a) of adsorbed substance, which means that the quantity adsorbed is independent of the total quantity dissolved. A little reflection will show that this condition is naturally only fulfilled with certain limits.

For anomalous adsorption the Freundlich equation would have the exponent 1

$$\frac{v}{m}\log\frac{a}{a-x} = a\left(\frac{a}{v}\right)^{-1}$$

$$i.e.\ \log\frac{a}{a-x} = a\,.\left(\frac{m}{a}\right)$$

In this case, therefore, x is a function of a but not of v, an assumption which is legitimate in a wider sense than the previous one.

TABLE III.

SOME ADSORPTION CONSTANTS FOR ANIMAL CHARCOAL.

Since the same kind of charcoal was used in each case, the constant k or α is an approximate measure of the "adsorbability" of the substance; k and $\frac{1}{p}$ are the constants of the ordinary equation, α and $\frac{1}{n}$ those of the Freundlich equation.

	k	$\frac{1}{p}$	α	$\frac{1}{n}$	Author.
Formic acid . . .			2·366	0·549	H. Freundlich
Acetic acid	2·606	0·425	2·999	0·526	"
Propionic acid . . .	3·463	0·354	3·784	0·606	"
Butyric acid . . .			4·977	0·699	"
Monochloracetic acid			4·375	0·637	"
Dichloracetic acid .			5·916	0·553	"
Trichloracetic acid .			3	0·7	"
Succinic acid . . .	4·426	0·274	4·656	0·757	"
Citric acid			4·385	0·83	"
Benzoic acid . . .			19·23	0·662	"
m Nitrobenzoic acid .			43·4	0·511	"
Picric acid			4·955	0·760	"
Benzene sulphonic acid			2·042	0·777	"
Acetone	5·212	0·52	2·74	0·444	L. Michaelis & Rona
Glucose			1·02	0·61	"
Crystal violet . . .			593	1·11	Freundlich & Losev
New fuchsine . . .			906	0·814	"
Patent blue			253	0·81	"

CHAPTER III

THE SURFACE AS THE SEAT OF ELECTRICAL FORCES

9. **Introductory.**—Generally speaking, every surface separating two phases is the seat of electrical forces. It is usual to distinguish between frictional electricity and contact electricity, and it is therefore necessary to consider both kinds in our treatment of surfaces.

From the modern point of view the difference between the two forms may be expressed by saying that the material carriers of contact electricity, which are responsible for all galvanic phenomena, are the ions, while the method of transport of static or frictional electricity is not so well understood. Thus, in striking contrast with the historical development of our knowledge of the two forms, the phenomena of contact electricity, which can be generally classified as ionic electricity, are now much more clearly understood, and it is with these phenomena that we shall be mainly concerned. It must not be assumed, however, that frictional electricity does not play an important part in biological process. Where a phase in a state of fine subdivision is floating in a liquid medium, opportunities for the generation of frictional electricity are amply provided by the movement of the particles against the liquid, which may be caused by convection currents, by shaking, or even by Brownian molecular movement.[1] It is only, however, in the case of ionic electricity that we have a clear idea of the mechanism involved, and this form will therefore receive most of our attention in the following discussion.

Many atoms and groups of atoms possess the property of becoming charged with electricity, and the quantity of electricity which is attached to an atom or group is determined just as it would be if electricity were a chemical substance which could form atoms, *i.e.* the laws of constant and multiple proportions are applied. We may therefore add, as Nernst does, two new elements to the ordinary list, the positive electron $\oplus$ and the negative electron $\ominus$. These can combine to form a neutral electron according to the equation $\oplus + \ominus \rightleftharpoons \boxed{+-}$. The facts and hypotheses which lead to this view are due particularly to Faraday, Helmholtz, and Arrhenius, while the resulting atomic conception of electricity has been developed by Nernst.

Whatever view be taken of the actual truth of Nernst's hypothesis, it is a valuable working tool for physico-chemical purposes, and it furnishes an interpretation of all the facts of contact electricity. We can therefore attempt to represent the affinity of the various atoms for the atoms of positive or negative electricity in the same way as chemical affinity, and apply to it the law of mass action. If we take the constant of the law of mass action as a measure of this affinity we obtain an equation such as the following :—

$$k[\mathrm{A}] \, . \, [\oplus]^n = [\mathrm{A} + + \ldots]$$

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[1] J. Perrin, *J. Chim. phys.*, (1904) **2**, 50.

Here [A] represents the concentration of free atoms, $[\oplus]$ the concentration of free electrical particles, *n* the valency, and $[A++\ldots]$ the concentration of the ions of valency *n*. Since the free particles of electricity can only result from the very slight dissociation of the neutral electrons $(+-)$, the concentration of free particles is proportional to the square root of the concentration of the neutral electrons. The neutral electrons are believed to be present in very large quantities in all bodies, so that the concentration of the free electrical particles may always be considered as constant, and the equation becomes simplified to

$$k[A] = [A++\ldots]$$

i.e. for a particular kind of ion the concentration of the ions has a characteristic ratio to that of the uncharged atoms. The quantity *k* is the affinity constant. In comparison with other affinity constants, electrical affinity constants of this type appear to be generally extremely small, but they have very different values for different atoms.

In any case, however, we may assume the existence of an "affinity" as defined in the above sense between atom and electron.

10. The differences of Potential between Simple Metallic Surfaces and Solutions.

—If we start with the usual simple example, *i.e.* a pure metallic surface such as silver immersed in a liquid, we are dealing with a two-phase system, and if the liquid chosen is a dilute solution of a silver salt, then both phases contain silver atoms and silver ions. Although the concentrations of silver ions in the metal and of electrically neutral silver atoms in the solution are both extremely small, there is nothing to prevent their values being used in a theoretical treatment of the subject, provided that they are quite sharply defined. Now if a simple chemical substance is divided between two phases the partition takes place according to the following general law. The concentration of the substance in one phase bears a definite ratio to its concentration in the other (Henry-Nernst partition law). This ratio is called the "partition coefficient" of the substance. We can foresee to some extent the magnitude of the partition coefficients of the substances we are now considering. The quantity of ionised silver in the metal is so small that it has not yet been directly detected, while the quantity of silver ions in the solution may be considerable. The partition coefficient of the ions in the direction silver-water is, therefore, nearly zero. Conversely the partition coefficient of electrically neutral silver atoms is practically infinite, or in other words the silver ions in the system are almost entirely in the solution, while the silver atoms are almost entirely in the metal. The equilibrium of the electrically neutral atomic silver is therefore given by

$$\frac{[\mathrm{Ag}]}{[\mathrm{ag}]} = k_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The quantities in brackets represent the concentrations of the corresponding particles, Ag representing the molecule of metallic silver, ag the atomic unionised silver in the solution. From the law of mass action

$$[\mathrm{ag}] = k_2 [\mathrm{ag}^+] \quad . \quad . \quad . \quad . \quad (2)$$

$[ag^+]$ representing ionised silver in the aqueous solution. If we substitute the value of $[ag]$ from equation (2) in equation (1) we get

$$\frac{[Ag]}{[ag^+]} = k_1 . k_2 = k_3$$

which means that the concentration of the silver atoms in metallic silver bears a constant ratio to the concentration of the silver ions in the solution. This constant is the relation between two measurable quantities, and from this point onwards it will be possible to neglect the unmeasurably small concentrations of ions in the metal and atoms of free metal in solution. The above constant k_3 we will write P, and it will be called the solution tension (Nernst), or the electrolytic solution pressure (Ostwald), of silver. It is comparable with the vapour-pressure of a liquid.

The above theory is not nearly sufficient to account for all the experimental facts. When a silver plate is immersed in water, practically no silver is dissolved in the ionised form, and when silver is immersed in excess of nitric acid the quantity dissolved is determined only by the solubility of silver nitrate in water and not at all by the above equation. There must, therefore, be a force at work which prevents the attainment of equilibrium according to the above law. This force is of an electrostatic character. When silver ions pass into solution from metallic silver, they carry away from the silver plate an enormous quantity of positive electricity (96,540 coulombs per gram-molecule), and a corresponding negative charge is left behind on the plate.

The two charges will attract each other with a very large force, and therefore we can imagine almost the whole process being reversed. The change will, in fact, only take place until the equilibrium is attained, *i.e.* until the electrical attraction is equal to the solution pressure. The process of solution, therefore, only proceeds to such a minute extent, that the dissolved metal cannot be detected by analytical methods, and in its place a correspondingly large difference of potential appears between the silver plate and the solution. On the basis of this argument we are in a position to calculate the magnitude of the difference of potential. It must be equal to the force with which the ions tend to pass into solution. This force depends in turn on the number of ions already in solution, and is at its greatest when the number of ions is least. It is apparent, therefore, that in order to have definite conditions, the solution must contain silver ions in definite concentration arising, for instance, from silver nitrate. In studying such a system consisting of a silver plate immersed in a solution of a silver salt, we may imagine a small quantity of silver becoming ionised and dissolved, without increasing the concentration of silver ions in the solution to a measurable extent. The new ions will be held in the immediate neighbourhood of the silver plate by electrostatic attraction, and will form a layer situated a minute but finite distance from the plate. Opposite to it on the plate will be a corresponding layer of free negative electricity. These two layers together form what Helmholtz has called an electrolytic double layer.

In order to calculate the difference of potential we will apply a method used by Nernst,[1] which is generally applicable in the determination of equilibria; we will assume the equilibrium point to be slightly overstepped. If the solution of the silver ions proceeds a little beyond the equilibrium point, the small quantity *dm* gram-molecules[2] of silver may be assumed to dissolve without altering the concentration of the solution to an appreciable extent. This means that *dm* gram-molecules of metal are removed from a place where their pressure is P (the electrolytic solution pressure) to a place where their pressure is p (the osmotic pressure of the dissolved silver ions), which involves the same amount of work as the expansion of *dm* gram-molecules of a gas from a pressure P to a pressure p. This work is $\mathrm{RT} \log \frac{\mathrm{P}}{p}$ per gram-molecule, and therefore in the case under consideration the work $d\mathrm{A} = dm\mathrm{RT} \log \frac{\mathrm{P}}{p}$. In reality, of course, this work is not done. If it were the process would be reversed by the consumption of an equivalent amount of electrical energy until equilibrium was again attained. Electrical energy is measured as the product of the quantity of electricity moved into the difference of potential (E).

Therefore

$$\mathrm{E}d\mathrm{F} = dm \,.\, \mathrm{RT} \log \frac{\mathrm{P}}{p}$$

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[1] W. Nernst, Die elektromotorische Wirksamkeit des Ionen, *Z. physik. Chem.*, 1889, 4, 129.

[2] The term gram-molecule means 108 grams of silver in the ionic or metallic condition, the particle of silver being monatomic in both cases.

or $$E = \frac{dm}{dF} \mathrm{RT} \log \frac{P}{p}$$

$\frac{dF}{dm}$ represents the electricity carried by one gram-molecule of the ion. For purposes of numerical convenience, we will measure the mass of the ionised substance not in the ordinary manner, but in multiples of a unit which carries one coulomb of electricity (*i.e.* $\frac{1}{96540}$ of a gram molecule). In this case $\frac{dF}{dm} = 1$ and

$$E = \mathrm{RT} \log \frac{P}{p}$$

It is, of course, necessary to measure the constant R in the same units as the mass of the ions. Nernst calculates that under these circumstances

$$R = 0{\cdot}861 \times 10^{-4}$$

Transforming natural into Briggsian logarithms,

$$E = 0{\cdot}000198 \log_{10} \frac{P}{p} \text{ volts}$$

The measurement of a single difference of potential offers great experimental difficulties, but it is quite easy to obtain the difference between two differences of potential, which is the electromotive force of a galvanic cell. If two electrode-systems are combined so that the metal plates are connected by a conducting wire, while the two solutions are in liquid contact, an electric current will pass if the differences of potential at the two electrodes are unequal. This is the case (1) when the two electrodes are of different metal, each immersed in a solution of one of its salts; (2) when the electrodes are of the same metal immersed in solutions of one of its salts of different concentrations; (3) when the metal and the solution are the same, but the metal is present in different concentrations in the material of the two electrodes (*e.g.* in the form of amalgams of different composition); and (4) when the metal and the solution are the same, but the electrodes are at different temperatures. The surface of contact between the two liquids can also exhibit a difference of potential, but this is usually very small, and has not been considered in the above argument.

If we can devise a method of determining P directly, it will be possible to calculate single differences of potential by means of the Nernst formula. Several such methods exist, but in view of the uncertainty of the results obtained by them up to the present, we will confine ourselves to the indication of their general principles. Helmholtz has shown that a mercury-dropping electrode will finally assume zero difference of potential against a solution of a mercury salt. Each drop of mercury becomes surrounded, as described above, with the electrolytic double layer and carries this to the bottom of the vessel. This process goes on till no more double layer is formed. Then the difference of potential becomes constant with a value of 0. Consequently if a galvanic cell is constructed with a dropping electrode and an ordinary electrode, it will have an E.M.F. equal to the difference of potential at the ordinary electrode. This principle was first applied by Ostwald, but the accuracy of the measurements is greatly affected by practical and theoretical difficulties, so that only approximate values are obtained. A second method depends upon the relation between difference of potential and surface tension, which will be considered later. A capillary mercury electrode in contact with a solution of a mercury salt has a potential difference of zero when the surface tension of the mercury has a maximum value. If this maximum is attained in contact with a solution of known concentration then the electrolytic solution pressure of the mercury can be obtained from the equation

$$\mathrm{RT} \log \frac{\mathrm{P}}{p} = 0$$

where P is the only unknown.

A third method worked out by Billiter,[1] allows of the identification of the zero point in the following manner. A particle of metal suspended by a fine thread and immersed in a solution of one of its salts is placed between the two electrodes of a circuit through which current is passing. According as the potential of the particle is positive or negative it will be attracted by the cathode or anode. By varying the concentration of the salt solution the sign and magnitude of the potential difference of the metal may be changed until it is not attracted either by the anode or the kathode. Under these circumstances the potential difference is zero.

Freundlich and Makelt[2] have shown that the method of Billiter is to some extent unreliable, since it gives rise to further differences of potential and measures them in addition to the one desired.

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[1] Billiter, *Ann. physik.*, 1903, 11, 902.

[2] Freundlich and Makelt, *Z. Elektrochem.*, 1909, 15, 161.

These methods give results which differ considerably among themselves, and as a satisfactory explanation of the differences is not yet forthcoming, the determination of a single difference of potential is a problem still to be solved. The Nernst formula for the determination of relative potentials has, however, been completely verified, so that the theory of the origin of potential differences between metals and solutions of their salts is also quite established. In our arguments, however, we shall often deal with single potential differences, and it is to be hoped that a reliable method for their determination will soon be discovered.

Theoretical note on the justification for the use of infinitesimally small concentrations in calculations.—In the foregoing arguments frequent use has been made of extremely small values for the concentrations of substances (*e.g.* the silver ions in metallic silver) which cannot be detected by experiment. It is desirable that some explanation should be offered for this method of reasoning. Although the experimental measurement of the extremely small quantities cannot be carried out, we are still at liberty to assume that they have real values. Even if the values are not real but only "imaginary," and if the substances assumed to be present in such small quantities have in reality a concentration of zero, nevertheless the conclusions drawn from the calculations agree perfectly with experiment, when they are extended into the region of measurable quantities. An example from electro-chemistry will make this clear. If a silver salt be treated with potassium cyanide, the silver ceases to exhibit the characteristic properties of silver ion and is mainly converted to the complex $\cdot Ag(CN)_2^-$ ion. This change is incomplete, being regulated by the law of mass action, but very nearly the whole of the silver ion disappears. If a small quantity of potassium cyanide be added to a known quantity of silver salt in solution, and the silver ion concentration determined by means of a concentration cell, it is then possible to calculate from the result obtained the concentration of silver ions which would be found in the presence of normal potassium cyanide. The value obtained is 10^{-32}. Making the usual assumptions with regard to the size of a molecule, this means that only three silver ions are present in 1 c.c. of solution, and if we take less than ⅓ c.c., then the probability is that no such ion at all is present. But if such a quantity of solution is tested by means of the concentration cell, the experimental value for the silver ion concentration agrees exactly with the very small number which would be expected from the calculation. We are not yet in a position to clear away this apparent contradiction,[1] and it is still open to doubt whether the extremely small measured value of the Ag-ion concentration corresponds to a real thing, or whether it is a mere number for purposes of calculation. Any calculations from this quantity, however, which have for their results finite numbers, are just as valid as if the minute quantity itself were really correct. For example, if we work out the value of the potential of a silver electrode against a solution containing concentrated potassium cyanide from the calculated value of the concentration of silver ions in that solution, we obtain the same result as we should get by direct experiment.

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[1] Haber, *Z. Elektrochem.*, **1904**, **10**, **433**.

In the same way one may doubt the real existence of silver ions in metallic silver, or of silver atoms in a solution of a silver salt, but the measurable consequences of the presence of this unmeasurable quantity are none the less true. The advantage of the assumptions is that they permit of the direct application to these electrodes of the partition law.

This hypothesis is only one form of a more general method of reasoning, which is of great value and which, if carefully used, cannot yield erroneous results. If we know from our experience of a suitably chosen analogous example, that a particular species of molecule is capable of existing, then to all intents and purposes it does exist. It may be present in very minute or immeasurably small concentration, but conclusions as to measurable quantities may be freely drawn from data which relate to the minute quantity. We may consider such minute quantities to be fictions, but they are notwithstanding, fictions from which real conclusions can be reached. It is entirely a matter of taste whether one would rather work with such fictitious quantities, whose meaning is clear, or with complicated mathematical functions, such as thermodynamic potential. They are only two methods of expression for the same thing, and it is probable that physiologists should be advised to choose the conception which can be most directly presented.

11. **Metallic Mixed Potentials.**—Up to this point we have only been concerned with the difference of potential when a single metal is immersed in a pure solution of one of its salts. It is now necessary to consider the state of affairs when both electrode and solution contain more than one metal. Suppose, for instance, a mixture of zinc and copper is immersed in a solution containing both zinc salts and copper salts. Then at first the zinc particles will have a fixed potential against the solution, and the copper particles another and a different potential. Such a state of affairs cannot, however, be permanent. If the copper potential is higher than that of the zinc, then the mixed potential will have a mean value, and the whole electrode will behave as if it had a lower potential than copper alone and a higher potential than zinc alone. But when by this process the difference of potential is brought to a value different from that which it would have with zinc alone, this value is not sufficient to put a stop to the emission of zinc ions, and consequently these ions pass into solution. On the other hand, the potential is too large for the copper equilibrium, and consequently copper is deposited from the solution.

As a result of the change in the composition of the solution the single potentials of the copper and the zinc are changed and they approach each other until they have the same value. When this point is reached there is nothing to produce further change, and equilibrium is set up, but during the attainment of equilibrium the difference of potential has not a fixed value but gradually changes with time. In this way we obtain the reaction

$$Zn + CuSO_4 \rightleftharpoons Cu + ZnSO_4$$

and the end of the reaction is reached when the two partial potentials are equal to each other. Now a zinc electrode in a normal solution of zinc sulphate has the same difference of potential as a copper electrode in a 10^{-38} normal solution of copper sulphate, so that a zinc copper electrode is in equilibrium with a solution which is normal with respect to zinc sulphate and 10^{-38} normal with respect to copper sulphate. This means that the less electropositive metal disappears practically completely from the solution, and is replaced by the more electropositive. The electrode behaves, therefore, when equilibrium is attained, as though it contained only zinc. Consequently in mixtures of metals, it is usually only the more electropositive metal which is responsible for the difference of potential. If the two metals do not differ very greatly as regards their solution pressures, it will be found that measurable quantities of both metallic salts remain in solution, and both metals may be said to be responsible for the potential difference.

A platinum surface charged with hydrogen behaves exactly as if it were composed of a modification of hydrogen, which conducts like a metal, platinum being much less electropositive than hydrogen. In this case, however, the concentration of the hydrogen in the platinum is of importance, since, when this concentration is increased, the solution pressure of the hydrogen is increased. According to the partition law the ratio of the concentration of hydrogen ions in the metallic phase to the concentration in the liquid phase has a definite value, and therefore the solution pressure of hydrogen is obviously proportional to the concentration of hydrogen ions in the metallic phase. These ions are only present in unmeasurably small concentration, and cannot be detected analytically. They may be looked upon, however, as resulting from the action

$$H_2 + 2\oplus = 2H^+$$

and so according to the law of mass action

$$[H^+]^2 = k[H_2]$$

i.e. the concentration of the hydrogen ions is proportional to the square root of the concentration of hydrogen molecules. It is thus possible to obtain a hydrogen electrode, which exhibits varying differences of potential against the same solution of hydrogen ion (acid), by bringing a platinum electrode into contact with hydrogen and raising or lowering the pressure (*i.e.* increasing or decreasing the concentration of the absorbed hydrogen). Two gases, which under similar conditions have very different solution pressures, could be obtained with identical solution pressures by dissolving them in platinum with suitable partial concentrations. Thus in the case of gases, mixed electrodes have true mixed potentials for which both constituents of the mixture are of importance. The principal characteristic of a mixed electrode, as compared with a single one, is that for the single electrode the potential difference which is set up at the first instance is the final one and does not change unless the conditions are changed. With mixed electrodes, however, a chemical change begins which often continues for a long time, and it is not until this change is completed that the difference of potential reaches its final definite value.

12. **Simple Binary Electrodes.**—The surfaces whose potentials we have hitherto considered, have been purely metallic, belonging to electrodes which could only give rise to positive ions. Gas electrodes which can only give one kind of ion are of the same type, *e.g.* hydrogen gives rise to positive ions only, oxygen to negative ions only.

We have now to consider surfaces which can produce at the same time both positive and negative ions. These are substances of electrolytic character which in aqueous solution are dissociated into ions. From a solid salt such as potassium chloride in contact with water, three kinds of molecular particle pass from the solid to the liquid phase, viz. KCl, K^+ and Cl^-. The solid salt contains undissociated KCl in greatly preponderating quantities, and consequently it would seem possible that only this substance passes directly into the water, the ions appearing merely as a result of the consequent dissociation. It can be shown, however, that the solid salt does actually contain ions although only in very small quantities. This conclusion depends on the experimental fact that in the fused state, and for a considerable range of temperature below their melting-points, salts exhibit a definite electrical conductivity which is quite similar to the conductivity of aqueous solutions.[1]

For instance, Faraday's law, that equivalent quantities of the various ions are liberated by equal quantities of electricity, is valid for solid salts as well as for solutions. Direct observation of the electrical conductivity of a solid salt is not always possible, but there is no distinct point at which the conductivity first becomes measurable. Barium chloride conducts quite well when fused, and still markedly just below its melting-point, while at lower temperatures it becomes impossible to detect its conductivity. Silver chloride, on the other hand, is a good conductor even at ordinary temperatures. Obviously, therefore, there is no gap between conducting and non-conducting salts, but a gradual transition corresponding to more or less pronounced electrolytic dissociation. The dissociation is, however, so slight that we cannot detect it except by conductivity or electrolytic methods. The experimental facts, however, justify the conclusion that solid salts possess an "electrolytic solution pressure" in addition to the ordinary solution pressure, and are capable of emitting ions directly into the solution. In this respect they are very similar to metallic electrodes, the main point of difference being that in the case of the salts only electrolytic conductivity and no "metallic" conductivity is possible. As a result of this difference salts play a part entirely different from that of metals in the construction of galvanic cells. So long, however, as we are only considering surface potentials (and not the actual passage of a current) this difference does not concern us.

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[1] Haber, *Ann. Physik.*, 1908, 4, 26, 917.

The theory of electrolytic electrodes has also been worked out by Nernst, and is a direct continuation of the theory of metallic electrodes.[1] We must first consider the stationary state in which equilibrium has been attained between water and salt, *i.e.* a solution has been produced which is saturated for the particular temperature under consideration. Suppose we are dealing with a salt BS which is dissociated in aqueous solution to form the two monovalent ions B^+ and S^-. According to the Henry partition law the equilibrium between the solid salt and the saturated solution is defined by the existence of a definite ratio between the concentration of undissociated salt in the solid phase and that in the solution. There is, however, an exchange of material between the B^+ ions of the solid salt and those of the solution, and according to the partition law the ratio of the concentrations of B^+ ions in the two phases must have a definite value. The concentrations of S^- ions in the solid and in solution are also subject to the same law. We have thus defined the position of final equilibrium. Such a state can only be reached, however, when the distribution coefficients of the two ions are, by a coincidence, equal to each other. In other cases the definition would require that unequal quantities of the anion and the kation should pass into solution. Owing to the action of electrostatic forces, however, the difference between the two quantities cannot become measurable, and we must therefore assume that the quantities of anion and kation in solution must be equal to each other. With regard to the actual values of the concentrations of the ions a certain amount of latitude is possible. If the concentrations chosen for consideration are such that the partition law is satisfied for the kation, then more anions may pass into solution. This process cannot proceed very far, since by its operation a potential difference accompanied by a double layer is produced. If, on the other hand, the partition law is satisfied for the anion it will be found that the kations are not in equilibrium. From these arguments it follows that of all the conceivable concentrations of the ions in the solution the ones which will be attained are those for which the potential difference due to the anions is equal to that due to the kations.

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[1] Nernst, *Z. physik. Chem.*, 1892, 9, 137.

The difference of potential due to the kations is

$$\mathrm{RT} \log \frac{\mathrm{P}^{\cdot}}{p^{\cdot}}$$

where $\mathrm{P}^{\cdot}$ is the electrolytic solution pressure of the kations, and $p^{\cdot}$ the osmotic pressure of the kations in solution. In the same way the difference of potential due to the anions is

$$-\mathrm{RT} \log \frac{\mathrm{P}'}{p'}$$

where P' is the solution pressure and p' the osmotic pressure of the anions.

Equilibrium is only attained when these two differences of potential are equal, *i.e.*

$$\mathrm{E} = \mathrm{RT} \log \frac{\mathrm{P}^{\cdot}}{p^{\cdot}} = -\mathrm{RT} \log \frac{\mathrm{P}'}{p'} \left(= \mathrm{RT} \log \frac{p'}{\mathrm{P}'}\right)$$

This expression determines not only the difference of potential but also the ionic concentration of the solution, since the concentration, and consequently the osmotic pressure, of the anion must be equal to that of the kation.

We can also rewrite $P^{\cdot}$ as the true osmotic pressure of the kations in the solid substance $\pi^{\cdot}$ multiplied by the distribution coefficient against water $k^{\cdot}$, and in the same way $P' = \pi' k'$ and consequently

$$E = RT \log \frac{\pi^{\cdot} k'}{p^{\cdot}} = - RT \log \frac{\pi' k}{p'} \quad . \quad (1)$$

Since, at any rate for dilute solutions, the ratio between osmotic pressures is equal to the ratio between the corresponding concentrations

$$E = RT \log \frac{C^{\cdot} k^{\cdot}}{c^{\cdot}} = - RT \log \frac{C' k'}{c'} \quad . \quad (2)$$

where $C^{\cdot}$ and C' are the concentrations of the two ions in the solid phase, and $c^{\cdot}$ and c' the concentrations in the liquid phase. If we know $k^{\cdot}$ and k' these expressions define the difference of potential between a solid electrolyte and its saturated solution, and also the ionic concentration of the saturated solution.

The concentrations of the ions in a saturated (or in any other) solution of an electrolyte are given by the law of mass action as follows—

$$\gamma[BS] = [B^+] \times [S^-] = c^{\cdot 2} = c'^2 \quad . \quad (3)$$

Here $[B^+]$ or $c^{\cdot}$ represents the concentration of the positive ion and $[S^-]$ or c' that of the negative ion. The equilibrium constant γ must obviously have a definite relationship to the partition coefficients $k^{\cdot}$ and k', otherwise the definition of the equilibrium in a saturated solution would be ambiguous. This relationship may be worked out as follows—

From (2)

$$\frac{k^{\cdot}C^{\cdot}}{c^{\cdot}} = \frac{c'}{k'C'}$$

and therefore $$k^{\cdot}k'C^{\cdot}C' = c^{\cdot}c'.$$

From (3) $$c'c^{\cdot} = \gamma c$$

where c is the concentration of the undissociated electrolyte in the aqueous solution. If we substitute this in the previous equation we get

$$k^{\cdot}k'C^{\cdot}C' = \gamma c$$

$$\gamma = \frac{k^{\cdot}k'C^{\cdot}C'}{c}$$

But the concentration C (or rather the corresponding osmotic pressure P) of the undissociated part of the electrolyte in the solid state bears a definite ratio to that in the aqueous solution c

i.e. $$k = \frac{C}{c} \text{ and } \gamma = \frac{kk^{\cdot}k'C^{\cdot}C'}{C}$$

$\frac{C^{\cdot}C'}{C}$ is the dissociation constant Γ of the solid salt, and therefore

$$\gamma = kk^{\cdot}k'\Gamma$$

or $$kk^{\cdot}k' = \frac{\gamma}{\Gamma}$$

in other words, the product of the three partition coefficients is equal to the ratio of the two dissociation constants.[1]

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[1] W. Nernst, *loc. cit.*; E. H. Riesenfeld, Konzentrationsketten mit nicht mischbaren Lösungsmitteln, *Ann. Physik.*, 1902 (4), **8**, 616.

We have thus obtained noteworthy relationships between (1) the dissociation constant of a salt in solution and its electrolytic solution pressure in the solid state, (2) the dissociation constant and the potential difference of the solid salt against its saturated solution, and (3) the three partition coefficients (of the anion, kation and undissociated salt) and the two dissociation constants of the salt (dissolved and solid). It is perhaps desirable to repeat the definitions which have been used in this chapter, making use of expressions which are now more intelligible.

The electrolytic solution pressure of a solid salt in reference to its kation (anion) is the osmotic pressure of an aqueous solution of the ion against which the solid substance has a potential difference of zero relative to the kation (anion). It may be defined in another way as the osmotic pressure of that aqueous solution of the ion which has no tendency to receive further ions from or to give up ions to the solid substance, or as the osmotic pressure of a true saturated solution of the ion, presuming that the attainment of the true limit of saturation is not opposed by the ordinary electrostatic forces.

NOTE.—To avoid misunderstanding, it must be remembered that concentration and osmotic pressure are only proportional to each other in dilute solutions. When we speak of the concentration of the undissociated salt in the solid phase, for example, it is clear that the conditions are far from being those of a dilute solution. It is therefore not the true concentration which comes into the above expressions, but an imaginary one which is proportional to the osmotic pressure, the proportionality factor being the same as that for dilute solutions. Although it is really more correct to avoid using the conception of osmotic pressure in relation to non-dilute solutions, and to substitute other terms,[1] it is not necessary to complicate matters in this way if the above correction is borne in mind.

There is another difficulty which may be dealt with at this point. When a salt is in contact with its saturated solution the concentrations of the ions in the solid differ from those in solution, and it might be argued that the resulting difference of potential is of the same character as a so-called diffusion potential which exists when two solutions of different concentrations come into contact. In such a case the difference of the potential results from the different migration velocities of the two ions, and consequently the migration velocity is a factor in the potential difference, whereas in the case of a salt and its saturated solution the migration velocities are not considered. The difference is explained as follows: when two solutions of different concentrations in the same solvent come in contact, diffusion actually takes place, and consequently one ion may proceed in advance of the other, thus producing a difference of potential. In the two-phase system (solid salt-saturated solution), however, there is no diffusion, and no difference in progress of the ions, so that the diffusion potential does not appear.

Haber[2] has shown in a quite different way that a difference of potential must exist at the surface separating a solid electrolyte from its solution. The fact that electrolytes are also conductors in the solid state has already been discussed, and Haber has shown that the conductivity is purely electrolytic, and therefore caused by the presence of ions, so that Faraday's law is also valid for solid electrolytes.

Consequently we have at a metallic silver surface a difference of potential against solid silver chloride of the same character as that against silver chloride solution. If we take an arrangement such as the following—

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[1] Compare van Laar, *Sechs Vorträge über das thermodynamische Potential* (Braunschweig, 1906).

[2] Haber, *Ann. physik.*, 1908, (4), **26**, 927.

Ag $\underset{a}{-}$ solid AgCl $\underset{b}{-}$ saturated solution of AgCl $\underset{c}{-}$ Ag

it is clear that from such a system in equilibrium no current will be obtained on making a metallic connection between the silver plates. Otherwise free energy would be obtained without the agency of a spontaneous change, which would be a contradiction of the second law of thermodynamics. There are in this cell three surfaces *a*, *b*, and *c*. At *a* there is a definite difference of potential and similarly at *c*, so that if the cell is to yield no current there must also be a difference of potential at *b*, equal to the difference between those at *a* and *c* but of opposite sign, so that the algebraic sum of the three differences of potential shall be zero, *i.e.*[1]

$$E_a + E_b - E_c = 0$$

or

$$E_b = E_c - E_a$$

If P_1 is the electrolytic solution pressure of the metallic silver against the solid silver chloride, P_2 the electrolytic solution pressure of metallic silver against the dissolved silver chloride, p_1 the osmotic pressure of silver ions in the solid chloride, and p_2 their osmotic pressure in the solution, then

$$E_a = RT \log \frac{P_1}{p_1}$$

$$E_c = RT \log \frac{P_2}{p_2}$$

therefore

$$E_b = RT \log \frac{P_2}{p_2} \cdot \frac{p_1}{P_1}$$

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[1] The differences of potential are measured in the following senses: E_a is Ag/solid AgCl, E_b is solid AgCl/solution, E_c is Ag/solution.

The "electrolytic solution pressures" of silver against solid silver chloride and against the solution are constant quantities, and their ratio may be called the partition coefficient of silver ions between the solid and dissolved silver chloride. Therefore for the difference of potential of the silver ions in solid silver chloride against those in solution we again get a formula of the form

$$E_{Ag} = RT \log \frac{\pi^{\cdot}k^{\cdot}}{p^{\cdot}}$$

Similarly the potential difference for chlorine ions between solid and dissolved silver chloride is

$$E_{Cl} = -RT \log \frac{\pi' k'}{p'}$$

and since the two differences of potential must be identical, we obtain as before

$$E = RT \log \frac{\pi^{\cdot}k^{\cdot}}{p^{\cdot}} = RT \log \frac{p'}{\pi' k'}$$

for the electromotive force of a solid salt against its saturated solution.

We may now undertake the task of deciding the sense of the potential difference between any readily or slightly soluble substance and its saturated aqueous solution. Where no other electrolyte is present in solution this is especially simple. In the case, for instance, of a solid acid in contact with its saturated aqueous solution, if the osmotic pressure of hydrogen ions in solution is $p^{\cdot}$, then the osmotic pressure of the anions p' must be equal to $p^{\cdot}$, since the total number of anions is always equal to the total number of kations. This assumption (that $p^{\cdot} = p'$) is at any rate justifiable when the solution is sufficiently concentrated for the very small number of hydroxyl ions, which are always present in water, to be insignificant in comparison with the number of acid anions. On the other hand, the osmotic pressure $(\pi^\cdot)$ of hydrogen ions in the solid acid, which though very small is a definite quantity, must be equal to the osmotic pressure (π') of the anions.

The formula

$$E = RT \log \frac{\pi^\cdot k^\cdot}{p^\cdot} = -RT \log \frac{\pi' k'}{p'}$$

then becomes simplified to

$$E = RT \log \frac{\pi}{p} k^\cdot = -RT \log \frac{\pi}{p} k'$$

where π and p represent the osmotic pressure of the kations (or anions) in the solid and the liquid phase respectively, or

$$E = RT \log \frac{\pi}{p} k^\cdot = RT \log \frac{p}{\pi k'}$$

from which we get

$$\frac{\pi}{p} k^\cdot = \frac{p}{\pi k'}$$

or

$$\frac{p^2}{\pi^2} = k^\cdot k'$$

$$\frac{p}{\pi} = \sqrt{k^\cdot k'}$$

The ratio of the ionic concentration in the saturated solution to that in the solid salt is therefore equal to the geometric mean of the partition coefficients for the two ions between the solid salt and water.

If it is desired to eliminate the quantity π which cannot be measured experimentally and substitute for it the "electrolytic solution pressure" of the ions in the solid acid

$$\begin{aligned} P^{\cdot} = \pi^{\cdot}k^{\cdot} \text{ and } P' &= \pi'k' \\ &= \pi^{\cdot}k' \end{aligned}$$

then

$$k^{\cdot} = \frac{P^{\cdot}}{\pi^{\cdot}} \text{ and } k' = \frac{P'}{\pi'}$$

and

$$\frac{p}{\pi} = \sqrt{\frac{P^{\cdot}P'}{\pi^2}}$$

i.e.

$$p = \sqrt{P^{\cdot}P'}$$

Thus the osmotic pressure of the kations (which is also that of the anions) in a saturated solution of an electrolyte is equal to the geometric mean of the electrolytic solution pressures of the ions.

We may now consider a very important special case, viz. a solution containing a second electrolyte which has one ion in common with the solid, *e.g.* a solution of silicic acid in hydrochloric acid or of ferric hydroxide in aqueous caustic potash. Without the foreign electrolyte the potential difference

$$E = RT \log \frac{\pi^{\cdot}k^{\cdot}}{p^{\cdot}} = RT \log \frac{p'}{\pi'k'}$$

or in terms of electrolytic solution pressures

$$E = RT \log \frac{P^{\cdot}}{p^{\cdot}} = RT \log \frac{p'}{P'}$$

If both silicic acid and hydrochloric acid are in solution the concentration of hydrions is no longer equal to the concentration of silicate anions, and if we call the concentration of hydrogen ions $p^{\cdot}_1$ and that of the silicate ions (which are diminished in number by the addition of the stronger acid) p_1', then

$$E = RT \log \frac{P^{\cdot}}{p^{\cdot}_1} = RT \log \frac{p'_1}{P'}$$

Since $p^{\cdot}_1 > p^{\cdot}$ and $p'_1 < p'$ it follows at once that the difference of potential is diminished by adding hydrochloric acid. If the addition is carried sufficiently far the value of the difference of potential may pass through zero and change sign. It is not possible to make a general statement as to whether this occurs before the solution is saturated with the second electrolyte. The case is similar to that of metallic electrodes. In some cases, *e.g.* Cu/$CuSO_4$ solution, it is very easy to make a solution of the salt of such a concentration that the difference of potential at the surface of the metal vanishes. In other cases, *e.g.* zinc, and particularly potassium, it is not possible to obtain an aqueous solution of the required concentration, and therefore such a metal is negative towards all aqueous solutions of its salts.

In the special case when $k^{\cdot} = k'$, when no second electrolyte is present possessing an ion in common with the solid substance

$$E = RT \log \frac{\pi}{p} k = RT \log \frac{p}{\pi k}$$

This is only possible when

$$\frac{\pi k}{p} = \frac{p}{\pi k} \quad \text{or} \quad p = \pi k$$

Then E = RT log 1 = 0, *i.e.* when the partition coefficients are equal to each other there can be no difference of potential. This conclusion is obviously correct, since the differences of potential arise only from inequalities between the partition coefficients.

In order to arrive at the sign of the charge we must return to a consideration of the nature of the electrical double layer. The outer layer will be formed from the more soluble ion, *i.e.* from that which when it is present in the quantity determined by the electrical equilibrium is in a still unsaturated solution. The inner layer will be formed of the other ion, which is in a supersaturated solution and would partially return to the solid but for the constraint of the electrostatic force. We can therefore assume that the solution takes the charge of the more soluble ion. Moreover, although we have no reliable means of determining the magnitude of the differences of potential, we can easily decide on the sign of the charge by observing the direction in which solid particles (when in fine suspension) move under the influence of an electric current. It has been shown experimentally that all sparingly soluble substances which have in a chemical sense an acid character (*e.g.* mastic, silicic acid, sparingly soluble acid silicates such as kaolin, clay, etc.) are negatively charged with regard to the water, and that all sparingly soluble substances which are chemically of a basic character (*e.g.* ferric hydroxide, alumina, thorium hydroxide, and many other metallic hydroxides) are positive with regard to the water. In the first class, therefore, we find that the hydrogen ion is more soluble than any of the anions; and on the other hand, the OH ion in the basic substances is more soluble than any kation. Therefore the most mobile ions, H˙ and OH′, are also the most soluble.

13. **Mixed Binary Electrodes.**—The most frequently occurring conditions are those in which a mixture of two (or more) solid electrolytes is in contact with its saturated aqueous solution. Under such conditions, it is quite possible—and, in fact, frequently the case—that the two electrolytes form a chemical compound, or double salt, giving rise to a new component in the mixture, since a new electrolyte is formed which must be looked upon as a single substance, the simpler salts only appearing to a limited extent as dissociation products. These cases are very complicated, but do not offer any difficulties of principle, so that it is not necessary to deal with them here. When we discuss a mixture of electrolytes it will be understood that the components do not react to form double salts. On the other hand, the whole solid system must form in itself a homogeneous phase, otherwise our whole method of treatment is invalid. We must not assume a mixture of (relatively) coarse mechanical particles, but one of practically molecular intimacy, resembling a solution, where, in spite of the intimacy of the admixture, no reaction between solvent and solute need take place. If some change such as hydrate formation takes place, it does not necessitate, in dilute solutions, any variation in our method of treatment. Solid substances can in fact form such mixtures, and van 't Hoff, who has called them solid

solutions, has shown that the dissolved substance behaves in the solid state just as in the liquid or gaseous state. It exerts an osmotic pressure, and will diffuse into other solid substances, etc.

The calculation of the difference of potential of such an electrode is based on the fact that all the partial differences of potential must be equal to each other. If the osmotic pressures of the two kations in the aqueous solution are represented by $p^{\cdot}_1$ and $p^{\cdot}_2$, in the solid phase by $\pi^{\cdot}_1$ and $\pi^{\cdot}_2$, and those of the corresponding anions by p'_1, p'_2, π'_1, and π'_2, then—

$$\begin{aligned} E = RT \log \frac{\pi^{\cdot}_1 k^{\cdot}_1}{p^{\cdot}_1} = RT \log \frac{\pi^{\cdot}_2 k^{\cdot}_2}{p^{\cdot}_2} &= -\, RT \log \frac{\pi'_1 k'_1}{p'_1} \\ &= -\, RT \log \frac{\pi'_2 k'_2}{p'_2} \end{aligned}$$

or

$$\begin{aligned} E = RT \log \frac{P^{\cdot}_1}{p^{\cdot}_1} = RT \log \frac{P^{\cdot}_2}{p^{\cdot}_2} &= -\, RT \log \frac{P'_1}{p'_1} \\ &= -\, RT \log \frac{P'_2}{p'_2} \end{aligned}$$

From this formula, if $k^{\cdot}_1$, $k^{\cdot}_2$, k'_1, and k'_2 are known as well as E, the concentration of the solution can be determined; if the concentration and E are known, then the partial coefficients can be determined. For the concentration of the different ions we obtain the equilibrium condition—

$$\frac{k^{\cdot}_1 \pi^{\cdot}_1}{p^{\cdot}_1} = \frac{k^{\cdot}_2 \pi^{\cdot}_2}{p^{\cdot}_2} = \frac{p'_1}{k'_1 \pi'_1} = \frac{p'_2}{k'_2 \pi'_2} = X$$

or

$$\frac{P^{\cdot}_1}{p^{\cdot}_1} = \frac{P^{\cdot}_2}{p^{\cdot}_2} = \frac{p'_1}{P'_1} = \frac{p'_2}{P'_2} = X$$

and for the difference of potential—

$$E = RT \log X$$

14. **The Law of Equalisation of Potential.**—*Chemical Changes in accordance with the Law.*—From this law we know that solid electrolytes in contact with a liquid assume an exactly defined state of equilibrium. If we bring the substances into contact in quantities which do not satisfy the equilibrium conditions, *i.e.* which show no material equilibrium and no definite potential difference, then the material change will take place spontaneously. One or two such cases may be discussed.

The simplest kind of chemical change which is regulated by differences of potential has already been dealt with in studying the displacement of a metal from a solution of one of its salts by another metal.

In certain respects we may go into more detail. If a bar of zinc is immersed in a solution of cadmium salt which is free, or nearly free, from zinc salts, the potential difference at the metallic surface is relatively large, on account of the small number of zinc ions in solution. When the displacement is complete, and zinc has gone into solution, the difference of potential has greatly diminished. On the other hand, if we consider the arrangement as a cadmium electrode, then at the beginning, when there is no cadmium in the metal, the difference of potential of metal against the cadmium solution, if we change its sign, is extraordinarily large. At the equilibrium point the two differences of potential have so far approached each other that they have become equal.

A similar state of affairs holds for binary electrodes. If a solution of methyl violet, *i.e.* the chloride of methyl violet base (BCl), is treated with solid silicic acid in the form of kieselguhr, or of finely suspended "colloidal silicic acid," a chemical exchange takes place with the formation of almost insoluble methyl violet silicate at the surface of the solid phase, while an equivalent amount of hydrochloric acid goes into solution. If silicic acid is assumed, for convenience, to be a monobasic acid, the change is

$$SH + BCl \rightleftharpoons SB + HCl$$

The equilibrium point for this process is that at which all the differences of potential are equal to each other.

This law may be looked upon as the equivalent for chemical surface reactions of the law of mass action. Although a reaction may proceed in solution to a point of equilibrium determined by the law of mass action, when the reaction takes place at a surface the law of mass action can no longer be applied, since we cannot define the "active mass" of the reagents. Many dyeing processes are examples of such surface reactions. Even if the "active mass" of the dissolved substances is represented by the concentration, or by a simple power of the concentration, this method cannot be extended to the insoluble substances whose solid surfaces are reacting chemically with the solution. It might be argued that the active mass of the insoluble substance (*e.g.* silicic acid, animal or vegetable fibre) is defined by the definite, though minute, concentration of its aqueous solution, and that it may therefore be taken as a constant. This is frequently the case in applications of the law of mass action, but it is only possible where the actual reaction can be assumed to take place in the solution. When magnesia dissolves in hydrochloric acid, the reaction is probably preceded by the formation of a saturated solution of the sparingly soluble magnesium oxide which forms a thin film on the surface of the solid oxide and is continually renewed as it is removed. It is this film of solution which reacts with the hydrochloric acid. This case is characterised by the fact that the final product, magnesium chloride, is readily soluble in water. If the initial and the final product of a reaction are both insoluble, and only the third substance readily soluble, Nernst's argument, which depends largely on consideration of the diffusion velocity of the soluble end product, is no longer inapplicable. No doubt the law of mass action still applies in such cases, but it only gives information as to the concentration of the dissolved substances. For example, in the case of silicic acid and aqueous methyl violet solution, provided all the necessary data are known, the law of mass action will determine the concentration of the methyl violet silicate. This concentration, however, is practically zero, and is not one of the interesting factors in the reaction between silicic acid and methyl violet.

The law of equalisation of potentials, as we may call it, is consequently general for the surface reactions of ionic substances, and it has for such reactions an importance similar to that of the law of mass action which only governs the chemical processes taking place in a single phase.

One important point should be dealt with at this stage. It is impossible for the compositions of a phase at its surface and in its interior to differ permanently, apart from differences which are due to surface tension, and which are regulated by the law of maximum reduction of surface tension. To be precise, we may say that the composition of a whole phase is determined when the composition of its surface is laid down. If the surface tension is zero, then the interior will have the same composition as the surface. If the surface tension is not zero, there will be a slight difference, but this difference may always be exactly defined in terms of the composition of the surface. It is therefore necessary that a chemical reaction which has begun at the surface of a phase, shall proceed to the interior until the prescribed equilibrium has been attained throughout. But the rate at which the process spreads to the interior depends greatly on the viscosity of the phase. In perfect fluids it will be very rapid, and the state of equilibrium will be reached very soon. In a solid phase, however, the progress of diffusion is enormously impeded, with the result that the reaction appears, for all measurable intervals of time, to be confined entirely to the surface. This last type of reaction is fairly abundant, and has been called chemical, or electrochemical, "adsorption." When kaolin is dyed with a basic dye, the colouring matter only penetrates the outer layers. If the coloured materal is removed by a suitable solvent, the kaolin does not appear to diminish appreciably in quantity. It is not surprising, since the progress of the reaction towards the interior is so slow, that equilibrium is apparently attained when the thinnest layer of the surface is dyed. This does not in any way affect the value of our previous reasoning, although one further factor is involved which is worthy of mention. Under the above conditions there must be a diffusion potential between the outer layer of the kaolin and the interior. Although the diffusion process itself is very slow, the more rapidly moving ion of the newly-formed compound progresses more rapidly than the slower ion. Under the conditions of our example we have no means of detecting the existence of the diffusion potential, and in any case its value will be relatively small. The further the change penetrates towards the interior of the solid, the smaller the diffusion potential becomes, until when the true equilibrium is reached it has fallen to zero.

15. **Differences of Potential between Solutions of an Electrolyte in Different Solvents.**—When two different solvents, which are not entirely miscible with each other, containing the same electrolyte in solution, are brought into contact with each other, the ions of the electrolyte will distribute themselves between the two solvents according to the partition law. Various interesting cases present themselves for consideration in this connection. There may or may not be a definite difference of potential between the two solvents. We may also consider either cases in which the condition of equilibrium has been attained and all diffusion process is completed, or cases in which the concentrations are not yet adjusted and in which diffusion is still taking place.

In the simplest case, where there is no definite difference of potential between the solvents, and equilibrium has been attained, we can refer directly to the reasoning of the previous chapter. We have again

$$E = RT \log \frac{\pi^{\cdot}k^{\cdot}}{p^{\cdot}} = - RT \log \frac{\pi' k'}{p'}$$

defining both the difference of potential and the ratios of the quantities of each of the ions in the two solvents.

If one solvent has a definite difference of potential against the other, the same rules can be applied as in the case of binary mixtures of electrolytes. In this case the solvent is one electrolyte and the dissolved substance the other, and we obtain

$$E = RT \log \frac{p^{\cdot}_1}{k^{\cdot}_1 \pi^{\cdot}_1} = RT \log \frac{p^{\cdot}_2}{k^{\cdot}_2 \pi^{\cdot}_2} = - RT \log \frac{p'_1}{k'_1 \pi'_1}$$

$$= - RT \log \frac{p'_2}{k'_2 \pi'_2}$$

where $p^{\cdot}_1$, $p^{\cdot}_2$ are the osmotic pressures of the kations in one solvent, $\pi^{\cdot}_1$, $\pi^{\cdot}_2$ the osmotic pressures of the kations in the other solvent, and p'_1, p'_2, π'_1, π^{2}_{2}, the corresponding values for the anions.

It is probable that these conditions hold when a salt is added to a suspension in water of a substance which can dissolve the salt even in small quantities. Mastic, an electrolyte of an acid character, can dissolve small quantities of sodium chloride. Consequently if sodium chloride is added to a colloidal solution of mastic in water, the salt will diffuse into the mastic particles. If the partition coefficients of Na·-ion and

Cl′-ion between mastic and water are different—which is probably the case—then the addition of sodium chloride will bring about a change in the potential of the mastic particles against the water.

We may finally refer to the case in which the diffusion process which leads to equilibrium is not yet completed. If sodium chloride is suddenly added to a suspension of mastic in water, the salt will gradually diffuse into the solid or semi-solid mastic particles. A very thin surface layer becomes saturated at once, but the penetration of the salt to the interior takes a longer time. A difference of potential due to diffusion is set up, since the more mobile chlorine ion travels ahead of the slower sodium ion. This diffusion potential is not of very great interest here, however, since it does not affect the surface properties of the mastic.

16. **The impermeability of Surfaces to Ions, and the Non-diffusibility of Ions.**—Up to this point we have always assumed that, where there is a difference of potential at a surface, it is possible for an ion to pass from one phase to another. If the surface of separation between the phases is not permeable to one of the ions, our reasoning is considerably affected. Such cases are quite possible, and were first studied by Wilh. Ostwald.[1] The researches of Hamburger and Koeppe have shown that it is highly probable that the red blood corpuscles are not permeable to kations but only to anions.

Let us consider the simple case of a binary electrolyte with monovalent ions, dissolved with concentrations of c_1 and c_2 in two different solvents. When the two solvents are brought together it is to be assumed that the surface separating them is penetrable only by the anions and not by the kations. There will then be a tendency towards an exchange of material between the solutions, which will, however, be confined to the anions. These will tend to distribute themselves between the two phases in accordance with their partition coefficient.

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[1] W. Ostwald, *Z. physik. Chem.*, 1890, 6, 71,

This process cannot take place, since it would produce an inequality in the concentrations of positive and negative ions in a single phase. Consequently, as in all similar cases, an electrical double layer is formed at the surface, whose difference of potential is easily calculated. Suppose at equilibrium the concentration of the anions in one solvent is c_1, in the other c_2, and that the difference of potential is E. If we imagine that the point of equilibrium is slightly overstepped, so that a very small quantity *dm* of anion passes from one solvent to the other. The electrical energy obtained is E*d*F, where *d*F is the quantity of electricity carried by a quantity *dm* of the ion. The osmotic work which must be done is $dm\mathrm{RT}\log\frac{c_1k}{c_2}$, where k is the partition coefficient of the anion between the two solutions. At equilibrium the algebraic sum of these quantities of energy is zero, so that—

$$\mathrm{E}\,.\,d\mathrm{F} - dm\mathrm{RT}\log\frac{c_1k}{c_2} = 0$$

or

$$\mathrm{E} = \frac{dm}{d\mathrm{F}}\mathrm{RT}\log\frac{c_1k}{c_2}$$

Making the same assumption as on p. 54, we may write $\frac{dm}{dF} = 1$,

and $$E = RT \log \frac{c_1 k}{c_2}$$

It is characteristic of this equilibrium that it is determined only by the kind of ion to which the surface is permeable. The formula obtained is very similar to that of a single metallic electrode against a solution of a salt of the metal. In view of the fact that, according to the introductory definition, $c_1 k$ has a similar meaning to P (the electrolytic solution pressure of a metal), the formulæ are practically identical. The identity arises from the fact that a simple metallic electrode may be considered as a binary electrode, from which one of the ions cannot pass into the other phase. If we assume that the metal contains a small but definite number of positive ions, a corresponding quantity of negative electricity must be accounted for, not, of course, in the form of ions, but as free electrons. Free electrons can move about readily enough in metals—according to Nernst their movement is responsible for metallic conduction of electricity—but they cannot pass into solution or move about in solutions. It has been shown by Ostwald and Nernst[1] that conductivity in conductors of the second class (electrolytes) is entirely due to ions and not to free electrons.

The metal is therefore comparable with a solvent for the binary "electrolyte" whose positive ion is the metal ion and whose negative ion is a negative electron,

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[1] Ostwald and Nernst, *Z. physik. Chem.*, 1889, 3, 120.

The difference of potential of such an electrode (see p. 67, equation 2) is—

$$E = RT \log \frac{c_1 k}{c_2}$$

or

$$E = RT \log \frac{p_1 k}{p_2}$$

If for $p_1 k$ we write P, representing the electrolytic solution pressure, which is the same thing, we obtain—

$$E = RT \log \frac{P}{p_2}$$

in complete agreement with the result obtained on p. 54.

It is possible to imagine cases intermediate between the one first considered, where the exchange of ions is quite free, and the last one, where only one ion could pass. The movement of the second ion may be very considerably impeded, but not entirely abolished, so that the impermeability of the surface to this ion is only relative. In such cases, at the instant when the two phases are brought into contact, the transactions only concern the easily penetrating ion, and the difference of potential is that due to this ion—

$$E = RT \log \frac{P}{p}$$

After a sufficient time the potential will change, and finally attain the value—

$$E = RT \log \frac{P'_1}{p'_1} = -RT \log \frac{P'_2}{p'_2}$$

Such cases can only occur when the diffusibility of one ion is very greatly inferior to that of the other. Possibly such substances as silicic acid, glass, and kaolin would fulfil this condition. Silicic acid anion has certainly a very low diffusion constant, and Freundlich,[1] is of the opinion that on this account it is not possible to get a saturated solution within a measurable time when water and glass are brought into contact. This is based on experiments by Barus, who found that at high pressures and temperatures glass was strongly attacked and dissolved by water. If this view is correct, then the silicate ion will play no part (at any e in reasonable intervals of time) in determining the ifferences of potential which result from bringing solid cic acid (glass, kaolin, etc.) into contact with water.

17. The Mechanical Adsorption of Electro-es.—*Adsorption Potential.*—It is now necessary to urn to the consideration of mechanical adsorption, d to study the state of affairs when the adsorbed bstance is a highly dissociated electrolyte. Since ctrolytes are to a considerable extent decomposed into ns when dissolved, we must look upon their solutions being mixtures of two or, if we include the undis-ciated portion, of three different adsorbable substances. such a case their reciprocal effects in the process of sorption (see para. 6) must be considered. Each of three kinds of molecule will possess its characteristic ir of adsorption constants, and they will tend to adsorbed to different extents. This is, however, not sible as far as the ions are concerned, since the action the electrostatic forces demands that positive and tive ions shall be present everywhere in equal bers. Consequently a state of equilibrium will be

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[1] *Z. physik. Chem.*, 1907, 57, 385.

attained, in which the concentrations of anion and of kation in the adsorption layer are equal to each other, and at the same time the concentrations in the solution, though different from those in the adsorption layer, are also equal. Separation of positive from negative ions, owing to their different adsorption constants, will only take place to an infinitesimal extent, *i.e.* until the difference of potential produced by their separation is just sufficient to compensate the tendency to separation due to adsorption. If all the three types of molecule are readily adsorbed, the conditions are rather complicated, and the simplest case to consider is one in which two of the substances have no appreciable influence on the surface tension of water, and are therefore not adsorbed, only the third substance being adsorbable. If, for example, the ions are not adsorbed, and the undissociated substance is, the latter can pass without interference into the adsorption layer. At the same time the adsorption layer must become richer in ions, because the increased quantity of undissociated salt must, according to the law of mass action, give rise to an increased quantity of ions. If one of the ions tends to be adsorbed, and the other ion and the undissociated molecule do not, the adsorbable ion carries with it into the adsorption layer some of the other ion, and is consequently adsorbed to a smaller extent than if it were alone. Finally, when all the ions and molecules are appreciably adsorbable, the case becomes s
more complicated. In the first place, each of
different components of the mixture has a retard
effect upon the adsorption of the other compone

which cannot be represented in a formula (see para. 6). In the second place the electrostatic forces resist any separation of the ions which might be demanded by a pure adsorption equilibrium; and thirdly, a difference of potential is set up to represent the suppressed transport of material. If we wish to make any calculation of the magnitude of the difference of potential we must confine our attention to very dilute solutions in which the effect of one substance on the adsorption of another is not appreciable. Let us consider the electrolyte BS dissolved in water, and practically completely dissociated so that the concentration of each ion is c. If there were no interference by the electrostatic forces, the process of adsorption would produce a surface layer containing the ion B^+ with a concentration c_1, and S^- th a concentration c_2, leaving in solution the concenons c'_1 and c'_2, where c'_1 is not equal to c'_2. But tual practice the ions must be of equal concentra- at every part of the system, so that in the surface r the concentration of both ions is c_3, a value rmediate between c_1 and c_2, while in solution it is ntermediate between c'_1 and c'_2. To calculate the erence of potential the equilibrium is assumed to be eded in such a way that further dm gram molecules the ion B^+ are adsorbed. From this process the otic work $dm\text{RT} \log \frac{c_1}{c'_1}$ can be obtained. In the way, if dm gram molecules of the ion S^- passed the adsorption layer into solution, the work lable would be $dm\text{RT} \log \frac{c'_2}{c_2}$. In both cases the movement would be compensated by the expenditure of an equivalent amount of electrical energy. The dm gram molecules carrying a quantity of electricity dF, are carried back at a difference of potential E, the energy expended being therefore EdF.

$$\mathrm{E}d\mathrm{F} = dm\,\mathrm{RT}\log\frac{c_1}{c'_1} = dm\mathrm{RT}\ \log\frac{c'_2}{c_2}$$

and in the same way as before this can be reduced to

$$\mathrm{E} = \mathrm{RT}\log\frac{c_1}{c'_1} = \mathrm{RT}\log\frac{c'_2}{c_2}$$

so that on the one hand E, and on the other hand, c_1, c'_1, c_2, and c'_2, giving the data for the material equilibrium, are clearly defined.

Such differences of potential, which are due t inequalities in the adsorption of the ions, may be called adsorption potentials. Although they have not yet received much attention (except from Freundlich), there is no doubt that they are of frequent occurrence and considerable importance. It is probable that we hav in the adsorption of organic dyestuff by charcoal a ca where an "adsorption potential" can be observed und comparatively simple conditions. Methyl violet, fo example, is a strongly dissociated electrolyte. Its anio Cl, we may conclude from the behaviour of inorgani chlorides, to be not more than very slightly negativ adsorbed, since all chlorides raise the surface tension water in a similar manner. The dyestuff kation readily adsorbed, and consequently in the adsorpt of methyl violet an adsorption potential must be up. Experimentally it is found that the rate of se mentation of charcoal is changed by the addition of methyl violet, and of similar substances. This change is caused by a change in the surface tension, which is in turn, as we shall see later, dependent on the difference of potential.

It has already been shown that differences of electrical potential can bring about a displacement of material which must be classed as adsorption in its widest sense, and *vice versâ* it is now apparent that mechanical adsorption can give rise to differences of potential.

There is a very important consequence of this tion. It is unlikely that the adsorption constants for drogen and for hydroxyl ions are equal to each other. ey could only be so by a very remarkable coincidence. they are not equal the free surface of pure water must hibit a difference of potential against the interior. ere is no means of deciding whether this difference of tential exists at a free surface, but there is some idence in the case of the water-charcoal surface. arcoal particles move under the influence of an ectric current towards the anode, and are therefore gatively charged with respect to water. There is no pparent reason why the charcoal should be charged, it the above argument justifies us in assuming that e surface film of the water may be charged, and that charcoal particles are only moved by the pull of the ering film of water. The direction of this motion ees with the assumption that the hydroxyl is more ongly adsorbed than the hydrogen ion, since the arcoal is electronegative with respect to pure water.

18. **Chemical Effects of Mechanical Adsorption.**—We are now in a position to deal with another property of mechanical adsorption, namely its power of bringing about chemical decompositions. If charcoal, which is a purely mechanical adsorbing agent, is treated with a solution containing a salt of a heavy metal, or better still a basic dyestuff, the charcoal adsorbs only the basic constituent and not the whole of the dissolved substance. It adsorbs the base (not merely the kation) and leaves behind in solution an equivalent quantity of acid. From a solution of methyl violet, for instance, charcoal adsorbs the organic base, and the equivalent quantity of free hydrochloric acid is liberated. The chemical change has been produced as a result of the mechanical adsorption. The explanation of this phenomenon originally presented a great deal of difficulty, but on the basis of the laws discussed in previous sections, it is possible to obtain a fairly clear picture without any further assumptions. It is only necessary that the free base shall be more readily adsorbed than either the acid or the salt. In the examples quoted above, the free base is in all cases the least soluble constituent of the solution.

Amongst organic substances, it is practically always found that relatively insoluble substances are strongly bathotonic, *i.e.* readily adsorbed.[1] As an objection to this view it may be argued,[2] that it requires the methyl violet to be hydrolysed in solution, and t
such hydrolysis has not been detected and must c

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[1] Compare J. Traube, *Pflüger's Arch.*, 1904, **105**, 541.

[2] Freundlich and Losev, *Z. physik. Chem.*, 1907, **59**, 284.

equently be very slight. Such an objection, however, s not fatal. There must be some, if only a little, free ase in solution. All aqueous solutions contain ydroxyl ions, which are formed from water under all onditions. The solution of the basic dyestuff contains lso dyestuff kations F. When F· and OH′ ions are resent together the reaction

$$F^{\cdot} + OH' = FOH$$

ill take place and will continue to a state of quilibrium in which

$$[F^{\cdot}]\,[OH'] = k\,[FOH]$$

e. a certain quantity of free base will be formed. ince the base is readily adsorbed it will be partly emoved by the charcoal, and the above equilibrium ill be destroyed. More base will then be produced by rther hydrolysis of the dyestuff, and so on till the nal equilibrium is reached. Thus the effect of echanical adsorption is to increase the infinitesimally mall degree of hydrolysis of the dyestuff to an easily easurable amount, and apparently to cause the emical separation of the acid and the base. The nditions are, of course, complicated by the fact that e dyestuff bases belong undoubtedly to the class of bstances which are anomalously adsorbed. They rm surface membranes, and their adsorption is eversible; charcoal containing adsorbed methyl et does not give it up again to water, but only to hol. Probably the process is also peculiar, in the t that the dyestuff base is adsorbed by the charcoal h such a concentration, that it would be permissible to speak of the separation of a new solid phase. It is not accurate, therefore, to say that the problem of the behaviour of basic dyestuffs towards charcoal is completely solved.[1] The deficiency in the arguments is to be regretted, since if it were made good it would doubtless throw much light on what the author has called anomalous adsorption, and would consequently be of great biological importance.

19. **Relations between the Electrical Difference of Potential and the Surface Tension.**—It has been shown by Lippmann that if mercury, used as an electrode in a galvanic cell, is contained in a capillary tube, the position of the mercury meniscus in the capillary changes with the difference of potential used. Since the position of the meniscus depends only on the surface tension, it is natural to conclude that the galvanic polarisation has an influence on the surface tension. The arrangement of the apparatus for the experiment is essentially the following. An electric current is led into dilute sulphuric acid by means of an ordinary mercury electrode, and passes away through a second mercury electrode of capillary dimensions. The passage of the current may also be in the opposite direction. Since the sulphuric acid soon forms small quantities of mercury sulphate, the arrangement resembles a reversible electrode of the type studied by Nernst, in which a metal is immersed in a solut
of one of its salts. Such electrodes are gen
non-polarisable, *i.e.* they do not change their diffe

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[1] The explanation of Freundlich and Losev (*loc. cit.*) do
appear to be complete.

of potential against the solution when an electric current passes through the surface. In the cell, mercury-mercury sulphate solution-mercury, the passage of the current causes the solution of a certain number of mercury ions at one pole, and the separation of the same number at the other. Thus the concentration of the solution as a whole does not change, and therefore the difference of potential between the metal and the solution remains constant, provided that convection and diffusion currents keep the concentration of the electrolyte uniform. If one of the electrodes is in a capillary tube, the velocity of the currents is greatly diminished, and uniformity is not maintained. If mercury ions are passing into solution in the capillary, they will become concentrated in the neighbourhood of the electrode, so that the difference of potential between electrode and liquid is changed.

The theory of the connection between the magnitude of the difference of potential and the surface tension was worked out in part by Lippmann, and in a more exhaustive and fundamental manner by Helmholtz. The explanation is based upon Helmholtz's conception of the electrical double layer. According to this view the surface of the mercury is charged with positive or negative electrical particles. As in all conducting substances the charged particles are all in the surface layer, where they are driven by their repelling action on each other. A further consequence of the repulsion is that in the surface tself the particles attempt to separate themselves s far as possible, *i.e.* they enlarge the surface.

The electric charge is therefore opposed to the mechanical surface tension which tends to diminish the surface. Consequently when a surface has a difference of potential against its surroundings the value of the "total" surface tension will be reduced, and may even become negative. We can therefore distinguish between mechanical and electrical surface tension, whose algebraic sum is the total tension. For calculating the influence of the potential difference on the surface tension, Wilh. Ostwald's method, applying the principle of virtual work, is simpler than that of Helmholtz. A capillary electrode is assumed to possess a surface tension σ, with a difference of potential E. E is now increased to $E + dE$, causing σ to diminish by $d\sigma$. The loss of surface energy will be equal to the gain in electrical energy

$$F dE = - \omega d\sigma$$

$$\text{or } - \frac{d\sigma}{dE} = \frac{F}{\omega}$$

$\frac{F}{\omega}$ is the quantity of electricity contained in unit area of the surface when it exhibits a difference of potential E against its surroundings, *i.e.* it is the capacity of the surface.

The facts of capillary electricity remained for a long time unnoticed, except from the point of view outlined above, *i.e.* they simply explained the working of the capillary electrometer. Helmholtz had shown, it is true, that they might lead to the determination of absolute differences of potential, for when the difference of potential is zero, the surface tension must be at its maximum value, since either a positive or a negative charge would lower the surface tension.

In the field of colloid chemistry, however, these views have found a new application, which has not yet been completely worked out. Bredig[1] first pointed out that a lowering of the difference of potential between particles of metal in colloidal solution and the surrounding water must be followed by a rise in the surface tension, so that the flocculation of the suspended metal is encouraged. It is therefore of interest to inquire into the different methods by which the difference of potential of minute particles against water can be changed. It can be done in two different ways.

1. By bringing into a solution a salt which has an ion in common with the suspended metal (or sparingly soluble salt). If the suspended solid is an acid, then by adding a soluble acid or alkali to the water, we change the concentration of the hydrogen ion, causing a change in the potential difference, and consequently in the surface tension. If the suspended substance is a base, the same addition would produce an opposite effect.

2. By bringing into solution an electrolyte which can react chemically with the suspended substance. In the example previously quoted (p. 80), when solid silicic acid is added to methyl violet in solution, the chemical change leads to a new value for the potential difference.

It is also found that other neutral salts, which would not be expected on the above grounds to have any effect, produce changes in the surface potentials of suspended particles. The potential of ferric hydroxide, for instance, is changed by sodium chloride or sodium sulphate. This effect cannot be explained in either of the above ways, so it must receive special consideration. Let us take the example of colloidal ferric hydroxide, which is flocculated by the salts of the alkali metals, *e.g.* potassium chloride, because the potential of the colloidal particles is diminished.

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[1] Bredig, *Anorganische Fermente* (Leipzig, 1901).

The only satisfactory explanation which has yet been advanced for this behaviour is based on the assumption that potassium chloride is soluble, if only very slightly, in the solid iron hydroxide.

If the partition coefficients of the $K^{\cdot}$ and Cl' ions between water and the solid hydroxide are not equal, there will be a tendency for one of them to pass into the solid to a greater extent than the other. Electrostatic forces will prevent the actual separation, but in its place a new potential difference will be set up at the surface, which will produce an alteration in the magnitude of the original potential. The quantitative development of this idea has not yet been possible, as there is no way of measuring either the potential or the solubilities of the ions in the solid phase. The latter cannot be more than very minute in any case, so that attempts to determine them by the methods of chemical analysis will be fruitless.

There is another possible effect of neutral salts on the electrical potential of suspended particles, namely the production of adsorption potentials, when one ion is adsorbed to a greater extent than the other. This result can only be attained when the limiting surface has a measurable tension. Apart from charcoal and cellulose, most of the substances which readily form suspensions, in which they have a definite electric charge (*e.g.* ferric hydroxide, kaolin, etc.), have no measurable surface tension against the surrounding water. Consequently, in such suspensions there is no mechanical adsorption,[1] and adsorption potentials are not produced.

20. **Phenomena due to Frictional Electricity.**—All the phenomena considered up to this point have been concerned with ions. There are, however, other phenomena which are due either to the free electrons or to some other kind of ions whose character is not yet known. These are the phenomena of frictional electricity, which cannot be explained by the views considered in the foregoing sections. The opinion that the charges on many surfaces are of frictional origin is much older than the other, since frictional electricity was the first form to be discovered. It was much later that the way was opened (mainly by Nernst) for a real understanding of those forms of electricity which are to be attributed to the liberation of ions; but this understanding, when it did arrive, completely overshadowed the study of frictional electricity. The conditions for the appearance of frictional electrical effects are specially favourable in those cases which most interest us here. This is the case, for example, with substances in fine suspension or colloidal solution, which possess very large surfaces, and which move in contact with the water, either as a result of mechanical

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[1] Michaelis and Rona, *Biochem. Zeits.*, 1908–9, **15**, 210, and **16**, 490.

agitation, of convection currents, or of the Brownian movement. It is conceivable, and indeed probable, that the magnitude and sign of the resulting charge will depend upon the composition of the liquid, and especially upon dissolved material, as is the case with contact electricity. But in contact electricity, as studied by Nernst, the potential is determined only by the ions which can be emitted from the electrode, while in frictional electricity there is no reason for attributing a special effect to any particular kind of ion. Freundlich and Makelt,[1] for instance, have shown that the potential of silver powder falling through a column of water, varies with the nature and the concentration of the dissolved electrolyte. Silver salts, however, have no special effect, and $H^{\cdot}$, OH', $Mg^{\cdot\cdot}$ and many other ions produce changes of potential. The importance of such changes of potential in colloidal processes has only recently been emphasised by Freundlich, and the theory is still very defective. As a preliminary, we can only attempt to decide how far the above phenomena may be due to ions. Two of the subjects which we have previously discussed may be of importance in this attempt, viz. the differences of potential due to (1) mechanical adsorption of electrolyte, and (2) solution of an electrolyte in different solvents.

Such differences of potential at the surface are due to ions and not to electrons, but the ions of the electrode material have no special importance in fixing the difference of potential. It would be premature to develop this view further without the necessary experimental data, but it appears not unlikely that all the facts may be explained on ionic grounds. If this is the case, a final solution of the problem is possible, whereas the purely frictional potentials, in which we know much less of the carriers of the free electricity, are more difficult to explain.

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[1] **Über den absoluten Nullpunkt des Potentials, *Z. Elektroch.*, 1909, 15, 161.**

Among the important observations made in this subject by Perrin[1] are the following: The charge assumed by a solid particle against a liquid is greater for strongly ionised liquids than for feebly ionised ones. The ions of the liquid probably, therefore, take part in the production of the charge. The most active ions are $H^{\cdot}$ and OH', the former charging the solid particles positively, and the latter charging them negatively. $Na^{\cdot}$, $K^{\cdot}$, $Li^{\cdot}$, $NH^{\cdot}_4$, Cl', Br', I', ClO'_3 are only feebly active, the only active monovalent ions being $Ag^{\cdot}$ and $Tl^{\cdot}$. The polyvalent ions are more active, the activity increasing with the valency.

Freundlich[2] attributes the action of the ions to their adsorbability, and believes the potential to be an adsorption potential. If this is the case, the potential will be decided by the adsorption coefficients, and the ions may be arranged in descending series of activity as follows:—

Positive ions $H^{\cdot}$; $Al^{\cdots}$; $Cu^{\cdot\cdot}$; $Ag^{\cdot}$; $Na^{\cdot}$ $K^{\cdot}$.
Negative ions OH'; SO''_4; Cl' Br' I'.

21. **The Curvature of Surfaces.** — *Surface*

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[1] J. Perrin, *Comptes rend.*, Paris, 1904, 1^{e}, pp. 1388 and 1440, 2^{e}, pp. 513 and 564.

[2] Freundlich and Mäkelt, *loc. cit.*

Tensions in Colloidal Solutions.—On the basis of our observations up to this point we should state that the surface tension was not dependent upon the form of the surface, and therefore remained unchanged when the surface was bent or curved. This statement is quite justifiable under ordinary conditions, since the surface tension is due to the action of intermolecular forces, and the sphere of molecular attraction is very small indeed. Consequently if the curvature of a surface is not too great, those portions of it which are capable of attracting each other lie to all intents and purposes in the same plane. But if the distortion is considerable the state of affairs is changed. It has been observed by numerous experimenters[1] that as the curvature of the surface increases the surface tension increases. Very small drops, for example, have a greater surface tension than the same substance would have in its normal condition. (If the drops are extremely small the surface tension falls again, when the radius of the drop becomes less than that of the sphere of attraction of the molecules.) Such highly curved surfaces are formed when a very finely divided phase is distributed in a liquid, *i.e.* in the systems which Wo. Ostwald[2] has called "dispersiods." These systems, if the suspended particles do not tend to settle, are identical with the so-called colloidal solutions.

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[1] Lord Rayleigh, *Phil. Mag.*, 1890, 30, 285 and particularly 456. Willard Gibbs, *Scientific Papers*, London, 1906, vol. i. p. 242. Van der Waals and Kohnstamm, *Lehrbuch der Thermodynamik*, 1908, pp. 207 *et seq.* Reynolds and Rücker, *Phil. Trans.*, 1886, 177, 627. (See also Wo. Ostwald, *Grundriss der Kolloidchemie*, Dresden, 1909, p. 135.)

[2] *Loc. cit.*

Let us assume that the surface of the suspended particles, when they are in a particular condition, has a definite positive tension, due to mechanical and electrical causes. The effect of this tension will be to produce a diminution in the surface, that is a coalescence and enlarging of the drops. At the same time the mechanical surface tension of the suspended particles will become smaller, and consequently, if the difference of potential does not change, the total surface tension will diminish. Thus, when a given size of drop is reached the total surface tension may attain a value of zero. At this stage the tendency for the particles to coalesce disappears, since any further union would bring about a negative surface tension, and the particles would tend to divide till the tension again became zero. If, when the system is at its point of equilibrium, an electrolyte is added, which diminishes the difference of potential at the surface, the total tension again becomes positive, and further coalescence takes place. Therefore, when the physical conditions are otherwise favourable to the union or the separation of particles, we have a true equilibrium which is determined by the following conditions. The total tension in the surface of the suspended particles is always zero. A change in the difference of potential has for its final effect only a change in the size of the particle. If the potential difference is increased the particles will become smaller, and *vice versâ.*

It is quite probable that these are the conditions which prevail in the living organism. The cell content constitutes a colloidal solution, since it contains microscopic or ultramicroscopic particles of albumen or of albumen-lipoid compounds in a state of permanent suspension in a liquid medium. This cell system is subject to reversible changes under the influence of numerous electrolytes; sometimes it becomes clearer, sometimes more cloudy. Other properties of protoplasm (*e.g.* phenomena connected with stimuli) are closely connected with its state of distribution, so that the general behaviour of protoplasm suggests the existence of a mechanism similar to that just described.

APPENDIX

22. **Kinetics of Surface Reactions.**—We have hitherto only studied the reactions which take place at surfaces from the point of view of their final results, without reference to their velocities. We have, in fact, only sought to define the equilibria obtained. According to the general conception of chemical reactions we must assume that the reactions are generally reversible, and consequently equilibrium can only be defined kinetically as the state in which the velocity of reaction in one direction is equal to that in the opposite direction. In the same way, when mechanical adsorption takes place according to the principle of the maximum reduction of surface tension, we can define the point of equilibrium kinetically as follows. When in every short interval of time the number of molecules adsorbed is equal to the number which pass from the adsorption layer into the solution, the system is said to be in equilibrium. The same applies to electrochemical adsorption. Kinetic considerations, have, however, very little practical significance in these cases, because the changes take place so rapidly that equilibrium is reached instantly or in a very few minutes. There are, however, other reactions which take place at surfaces, which are not connected in any way with the specific properties of the surface. These reactions have been

studied principally by Nernst,[1] and their nature will be best understood by considering a typical example. If solutions of caustic soda and acetic acid are mixed, a well-known reaction takes place with the formation of sodium acetate and water. The course of this reaction, as of all ionic reactions, is extremely rapid, so that we cannot follow its progress, but only identify its conclusion. But if the practically insoluble oxide of magnesium is added to acetic acid the formation of the magnesium acetate takes an appreciable time. From analogy with other ionic reactions we are justified in assuming that the reaction in solution

$$Mg(OH)_2 + 2CH_3COOH = Mg(CH_3COO)_2 + 2H_2O$$

takes place instantaneously. The reason for the slowness of the process in practice is, that the dissolved magnesium hydroxide which must be formed before the reaction can proceed, is only very slowly obtained by solution of the magnesium oxide. The velocity of formation of magnesium acetate depends, therefore, only to a minute extent on the chemical change involved, and mainly upon the process of diffusion which brings together the newly formed magnesium hydroxide and fresh acetic acid at the surface of the solid. The theory of such reaction velocities has been developed by Nernst as follows. It may be assumed that in the immediate neighbourhood of the solid magnesia there is always a saturated solution of magnesium hydroxide, which is continually being renewed as it is used up by the acid. In this surface layer the solution will always be alkaline, however much acetic acid there may be in the bulk of the liquid. The reaction velocity will then be determined only by the time taken for the dissolved magnesia to reach the interior of the solution. The rate at which this takes place is dependent on external conditions; it is not only regulated by simple diffusion but also by convection currents produced by changes in the density of the solution. In order to obtain comparable experimental conditions such currents must be kept perfectly regular and constant in their action, which can be achieved by stirring at a constant rate. By varying the rate of stirring, the effect of the convection current can be varied at will. The velocity of the reaction depends also on the magnitude of the surface, and in order to obtain results of any value it is necessary to keep the amount of surface constant throughout the experiment. This is usually achieved by using the solid substance in the form of a large plate, which is uniformly attacked during the reaction with no appreciable change in its area. Under these conditions the reaction velocity at any instant is proportional, first to the area of the surface exposed, and second to the concentration of the acid in the solution. If we represent the initial concentration of the acid by a, the concentration at time t by $a - x$, the area of the surface by ω then,

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[1] W. Nernst, *Z. physik. Chem.*, 1909, 47, 52.

$$\frac{dx}{dt} = k\omega\,(a - x)$$

or integrated

$$\log \frac{a}{a - x} = k\omega t$$

The velocity coefficient k has been given a still more exact definition by Brunner.[1] When the stirring is sufficiently rapid it may be assumed that the composition of the whole of the solution, with the exception of the surface layer, is quite uniform. Close to the surface we have a very thin adherent layer of saturated magnesium hydroxide solution, which is alkaline. The further progress of the reaction consists in the diffusion of acid into this layer, which we may assume to have a thickness δ. The factors in the reaction are therefore the velocity of diffusion of the acid and the thickness of the surface layer. The velocity coefficient is, then, obviously proportional to the diffusion constant of the acid (D), and inversely proportional to the thickness of the layer—

$$k = \frac{D}{\delta}$$

and therefore $$\log \frac{a}{a - x} = \frac{D}{\delta} \cdot \omega \cdot t$$

Similar considerations can be applied where the rate of solution and not a chemical reaction of the solid substance is being investigated. This has been done by Noyes and Whitney in the following manner. If a solid crystal is suspended in water and the water is uniformly stirred, it may be assumed that the crystal is immediately surrounded by a layer of saturated solution, and if the stirring is carefully regulated, the bulk of the solution will always be of uniform concentration. The layer of saturated solution adheres to the crystal, even on stirring, but its thickness varies somewhat with the rate of the stirring. The velocity of solution under these conditions varies, first with the thickness of the surface layer which determines the length of the path of diffusion, and second, with the difference of concentration at the particular instant between the saturated surface layer and the remainder of the solution. If the concentration of a saturated solution is represented by C, and the quantity of substance which has become dissolved in time t by x, so that the concentration of the solution $c = \frac{x}{v}$, where v is the volume of the liquid, then

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[1] Brunner, *Z. physik. Chem.*, 1904, **47**, 56.

$$\frac{dx}{dt} = k(C - c)$$

But $c = \frac{x}{v}$, i.e. $dx = vdc$,

and therefore $$\frac{dc}{dt} = \frac{k}{v}(C - c)$$

or integrated $$k = \frac{v}{t} \cdot \frac{C}{C - c}$$

$C - c$ is the "saturation difference," k the velocity constant of solution, which depends upon the velocity of diffusion and the thickness of the adhering layer. Since the diffusion coefficients of many substances are accurately known, it is possible to calculate from the expression

$$k = \frac{D}{\delta}$$

the thickness of the surface layer for a given rate of stirring. Brunner found with his particular method of experiment δ for benzoic acid = 0·03 mm. This value will also hold for the case in which a chemical reaction and not mere solution takes place at the surface of solid benzoic acid. When the absolute values of D and δ are known, it is possible to calculate the velocity of solution of magnesia, for example, in different acids. These calculations have been made and the results completely confirmed experimentally by Brunner.

The influence of temperature on the velocity of solution appears to be considerable, and much greater than the influence of temperature on the diffusion constant. This can only be explained by assuming that the thickness of the adhering layer of saturated solution is greatly diminished by raising the temperature. This is also in accordance with the fact that the viscosity of water decreases very rapidly with rising temperature. With regard to the character of the surface, it may be remarked that the difficulty of obtaining perfectly smooth surfaces makes it impossible to measure accurately the extent of the real surface exposed by a given body. This difficulty is not of great importance, since the exact area of all the boundary faces is not identical with the actual working surface. The scene of the reaction is the surface layer whose volume is only slightly affected by small irregularities in the surface of the solid. The regulating factor is, therefore, not the microscopic character of the surface with all its roughness taken into account, but merely the area as determined from the ordinary dimensions. Consequently, if the irregularities are not great, the surface may be measured as if it were a uniform plane, sphere, etc.

In the above exposition it has been assumed for the sake of simplicity that the adhering layer was sharply defined from the rest of the solution. This is approximately true, but not exactly so, since the concentration falls steeply, but without discontinuity, from the surface layer to the main solution. If we consider more in detail the progress of solution with a constant rate of stirring, then in the immediate neighbourhood of the solution the concentration is AO = C. It then falls gradually as the distance from the surface (OS) is increased until it reaches the concentration c at the point B, by a course which may be represented as a first approximation by a straight line (AB). The process of solution is due to the diffusion of molecules from O to the point on the abscissa axis corresponding to B, whence it is further removed by the process of stirring. If the concentration (the ordinate in the diagram) be represented generally by C, the distance from the surface by s, then,

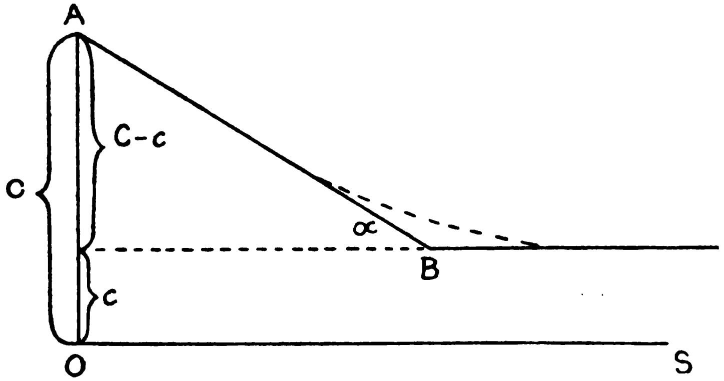

Fig. 8.

$$\frac{dx}{dt} = -D\omega\frac{dC}{ds}$$

where D is the diffusion coefficient. It follows from the figure that

$$\frac{dC}{ds} = \tan a = \frac{C - c}{\delta}$$

therefore

$$\frac{dx}{dt} = - D\omega \frac{C - c}{\delta}$$

If we now represent the facts more exactly by making the curve in the neighbourhood of B follow the dotted line, the argument is only modified by the difference in the value of δ. δ is no longer the true thickness of the layer, but a proportionality factor nearly corresponding to it, though not capable of exact definition. In any case the value found for δ will not differ greatly from the thickness of the layer.

The somewhat unexpected conclusion from this consideration is that the velocity of reaction in a heterogeneous system is mainly dependent on the rate of diffusion. Differences in chemical affinity disappear by comparison. Magnesia is dissolved more rapidly by the weak acetic acid than by the stronger benzoic acid, simply because the rate of diffusion of the acetic acid is greater. This fact is doubtless of great importance from a biological point of view.

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